Abstract

Layered chalcogenides, belonging to group III-VI and IV-VI, are considered to be potential candidates for mid-temperature range thermoelectric (TE) applications owing to their high power factors even at moderate carrier concentration, and intrinsically low thermal transport. In general, TE transport coefficients depend on the electronic structure of the materials, whereas, the thermal transport relies on their phonon band structure and density of states (DOS). Thus, detailed understanding of electronic as well as vibrational properties is required to elucidate the transport mechanisms in these systems. In this thesis the TE transport and thermal transport properties of three different layered chalcogenides such as, (i) SnSe-Cu_2Se phase separated alloy from group IV-VI, (ii) *n*-type In_4Se_3 from group III-VI, and (iii) another isostructural compound, *p*-type In_4Te_3, from the same group have been investigated. It is noticed that the alteration of the valance band occurs due to orbital interaction of Cu-d and Se-p electrons in the SnSe-Cu_2Se alloy, which results in the formation of secondary $SnSe_2$ phase as confirmed from the chemical potential map and Boltzmann transport theory. Modification of the DOS near the Fermi level also causes *n*-type conductivity in the alloy. The delocalisation of Se-lone pair, which is beneficial for low thermal conductivity, is due to large magnitude of atomic relaxation of Cu atom. The anisotropy in the Seebeck coefficient and its value are found to be lower in the alloy compared to those of the pure SnSe due to low DOS effective mass of the previous. The electronic part of the figure of merit (ZT_e) is notably larger in the alloy at low temperature and low carrier concentration ($n < 10^{21}$ cm^{-3} and $T \sim 350$ K). In SnSe, the carrier relaxation time is found to be dominated by electron – acoustic phonon interaction, whereas, in the alloy, it is due to electron-electron and impurity-electron interaction. In the next work, electronic structure of the *n*-type In_4Se_3 has been studied. It is observed that, at different doping level, the transport mechanisms of the carriers are determined by anomalous effect, Kane band, parabolic band and multi-band effect as we increase the doping concentration. Experimentally observed high Seebeck coefficient and other transport parameters of the system can be attributed to the Kane band transport at the moderate doping level. Moreover, the Kane band transport region shows constant ZT_e which eventually lead to overall high *ZT* (figure of merit). Iodine doped In_4Se_3 shows improvement in *ZT* due to high electrical conductivity and mobility. Then the effect of anti- and non-bonding rattler (In4) on the thermal transport of another isostructural compound, In_4Te_3, has been investigated in the framework of *Wigner transport formalism*. Our study suggests that the weakly bonded In4 interstitial atom results in significant anharmonicity and phonon mode softening in both the acoustic and low energy optical regions. The mean free path has already approached the Ioffe-Regel limit in space, even at low temperature, which is in line with the observed low κ_L. These softened Einstein like modes, which occurs around 72 cm^{-1}, form overlapped phonon band which promotes wave like tunnelling of the heat carrying phonons and subsequent unconventional wave-like thermal conductivity in the system.