ABSTRACT

The main focus of this thesis is to improve the thermoelectric figure of merit (*ZT*) in Cu_3SbSe_4 based materials and its composites by enhancing electrical parameters and reduction of lattice thermal conductivity. For higher *ZT*, its power factor ($= S^2\sigma$, where S and σ are the Seebeck coefficient and electrical conductivity, respectively) need to be enhanced or at least remained unaffected with the simultaneous reduction in thermal conductivity (k). For the experimental observation of the Zn substitution at Cu sites and its effect on thermoelectric properties in Cu_3SbSe_4, electrical and thermal transport properties in samples with different Zn contents have been investigated. A significant reduction in lattice thermal conductivity has been observed due to scattering of acoustic phonons via substitutional impurities in the crystal lattice with asymmetric occupancy of Zn at Cu site. As a result, enhancement in ZT value was achieved in $Cu_{2.5}Zn_{0.5}SbSe_4$ at 475 K due to the relatively higher value of Seebeck coefficient and the smaller value of thermal conductivity. For the reduction of thermal conductivity along with the increase in carrier concentration in Cu_3SbSe_4, Pb was used as a dopant. Thermal transport measurements coupled with microstructural investigation suggest that both increase in phonon scattering via grain boundaries, and structural defects on Pb doping play a significant role in the reduction of thermal conductivity. In this study, it is found that $Cu_3Sb_{0.05}Pb_{0.05}Se_4$ shows the highest *ZT* (~0.72 at 625 K), which is approximately two times larger than that observed in pristine Cu_3SbSe_4. The effect of nanoinclusion on the thermoelectric properties in Sn-doped Cu_3SbSe_4 based composite was studied. It was found that the enhancement in power factor and reduction in lattice thermal conductivity in Cu_3SbSe_4/Cu_2Se composite samples is due to the combined effects of low energy charge carrier filtering and scattering of phonon at the interfaces of Cu_3SbSe_4 and Cu_2Se. As a result, a maximum ZT with a value of 1.05 is achieved at 650 K in samples with 4 wt% Cu_2Se nanoinclusion. Anisotropic thermoelectric properties were studied in Sn, Bi co-doped Cu_3SbSe_4 samples synthesized at high pressure (75 MPa) via spark plasma sintering. Power factor was not found to be affected much as mobility shows anisotropic behaviour whereas carrier concentration remains the same in all direction. The thermal conductivity value was found different along the cross-plane and in-plane directions, whereas Seebeck coefficients in all the samples show almost isotropic behaviour and are independent of the directions of measurement. In our study, $Cu_3Sb_{0.97}Sn_{0.02}Bi_{0.01}Se_4$ show a ZT value of 0.92 along the cross-plane and 0.57 along the in-plane direction. We have demonstrated that the electrical transport characteristics of Cu_3SbSe_4/PEDOT:PSS hybrid nanocomposite film can be manipulated by the controlled inclusion of Sn-doped Cu_3SbSe_4 in PEDOT:PSS. The carrier concentration in PEDOT:PSS was found to decrease towards its optimum value with the addition of $Cu_3Sb_{0.98}Sn_{0.02}Se_4$. A maximum power factor of 164 $\mu Wm^{-1}K^{-2}$ has been realized at 420 K for the film with 4 wt% Sn doped Cu_3SbSe_4 ($Cu_3Sb_{0.98}Sn_{0.02}Se_4$). This value of power factor in composite film is significantly lower than that of its inorganic counterpart, however, the inorganic-polymer hybrid composite structure in Cu_3SbSe_4/PEDOT:PSS will favour the large area manufacturing which will further enable the high-throughput fabrication of low-cost and efficient organic thermoelectric generators.

Keywords: Thermoelectric, Seebeck coefficient, phonon scattering, figure of merit, nanograin, anisotropy, carrier concentration.