ABSTRACT

Research on crystal growth and characterization is inevitable to meet the requirements of the technological world, as there is a great demand for good quality samples free from flaws for application in various fields which cannot be met by natural resources. The synthesis of bulk crystals of Sb_2Te_3 compounds has intrigued the attention of the researchers in the present work, due to their diverse properties which provide boundless scope to develop innovative approaches towards the development of devices with improved thermoelectric (TE) efficiency. The green technology of conversion of waste heat to electric current by the TE phenomena offers a noise-free alternative with low mechanical and conduction losses for small scale refrigeration and power generation modules. Though, thermoelectric devices offer better reliability and durability, one of the major challenges is to develop a material system with high figure of merit (*ZT*) in the variable temperature ranges. From the research reports it is evident that, generally for scientific studies, conventional melt methods were used to grow bulk Sb_2Te_3 crystals, where nonstoichiometry, polycrystallinity and multi-phase formation raise problems. Furthermore, large fluctuations in TE properties have been exhibited by single crystals synthesized from the melt, which preclude their uses in devices. The ability to control as well as engineer various properties of Sb_2Te_3 depends on the choice of growth method, experimental tools and processes. Even though substantial work has been published on the studies of cleaved samples of crystals grown from the melt, the growth mechanism and TE investigations on vapor deposited platelet structures of $Sb_2Te_{3-x}S_x$ and $Sb_{2-x}In_xTe_3$ have not been investigated so far. With the prime focus on vapor deposition as an alternative to melt methods to produce defect free, good quality

stoichiometric and mechanically stable crystals with improved *ZT*, the research was aimed at growth and characterization of Sb_2Te_3 and related thermoelectric materials.

The approach towards the set targets of the present work adopts the effective and economically viable physical vapor deposition (PVD) process to grow good quality Sb_2Te_3 crystals with the aid of an indigenously fabricated dual zone furnace. Annealing, ^{60}Co gamma ray irradiation, sulfur and indium doping are the strategies utilized in the current work for improvement of TE properties. The optimization of temperature gradients could yield $Sb_2Te_{3-x}S_x$ and $Sb_{2-x}In_xTe_3$ samples of compositions, x = 0, 0.1, 0.2, 0.3 & 0.4 in the form of platelets.

By employing various sophisticated analytical tools such as X-ray diffraction analysis (XRD), energy dispersive analysis by X-rays (EDAX), scanning electron microscope (SEM), atomic force microscope (AFM) and transmission electron microscope (TEM), the structure, morphology and quality of the as-grown crystals were analysed. The thermoelectric parameters have been evaluated with the aid of Hall effect measurement system, van der Pauw method, differential scanning calorimetry, laser flash technique, etc. Vickers indentation testing and chemical etching were utilized for the estimation of microhardness and defect analysis of the samples.

Crystals grown by PVD in the present study were found to posses good mechanical strength, smooth surfaces, less substructure and imperfections than those reported by chemical as well as melt methods. The Seebeck coefficient of Sb_2Te_3 crystals was increased upon doping with sulfur and indium, which favored the enhancement of power factor (*PF*). The undoped Sb_2Te_3 crystals grown by PVD have shown a 46.6 %

increase in ZT compared to the conventional melt grown samples and the $Sb_2Te_{1.7}S_{0.3}$ delivered the highest figure of merit (ZT = 0.53) which is ~ 2.5 fold rise compared to the pure Sb_2Te_3 crystals. Thus, the vapor growth of Sb_2Te_3 and related TE materials from vapor is being recognized as a potentially transformative experimental process which can be scaled up for the development of cost-effective, environmentally green energy conversion systems.

The thesis is divided into seven chapters. Chapter 1 provides an introduction to the impact of thermoelectrics (TE) in science and technology. This chapter also includes relevant theories of crystal growth and the literature survey related to group V-VI semiconductors, status of antimony telluride (Sb_2Te_3) compounds and their applications. Various instruments and techniques employed for the preparation and characterization of Sb_2Te_3 crystals are explained in chapter 2. Chapter 3 is devoted to the synthesis of compound charge and growth of pure & sulfur doped Sb_2Te_3 samples of different morphologies, under various temperature gradients. The computation of TE parameters, figure of merit as well as Vickers microhardness is highlighted. The investigations on the growth and physical properties of indium doped Sb_2Te_3 crystals by the PVD method are emphasized in chapter 4. Chapter 5 deals with the influence of annealing and ^{60}Co gamma irradiation on the transport properties of the samples. Studies on optical transmittance and band gap of the grown crystals are reported in chapter 6. A brief account on the summary and scope of the work done is given in Chapter 7. Conclusions are outlined at the end of all chapters, highlighting relevant scientific aspects pertaining to the contents in addition to the bibliography.