

Climate change is a subject of deep distress in today's world. Over dependence on hydrocarbon has resulted in serious environmental problems. Rising sea level, global warming and ozone layer depletion are the mainstream of any discuss world over. The collective goal of cutting carbon emission by the year 2020 has prompted the search for clean, alternative energy sources. This effort are already yielding good reward as other forms of energy such as solar, wind, nuclear and hydro have received huge investment and renew interest over the past decade.

Thermoelectric materials over the past decades have been tipped to replace conventional means of power generations as these materials have the ability to convert heat to electrical energy and vice versa. They are simple, have no moving parts and use no greenhouse gases. But the major drawback of these materials is their low conversion efficiency. Hence there is a need to enhance the efficiency of thermoelectric material to fulfill their undeniable potentials.

A parameter called the thermoelectric figure of merit, ZT defines the efficiency of a thermoelectric material. ZT relates three non-mutually exclusive transport properties namely Seebeck coefficient, electrical conductivity and thermal conductivity. Efficient thermoelectric material should possess high Seebeck coefficient, high electrical conductivity and low thermal conductivity. Hence, one of the interesting ideas in the area of thermoelectric research is the concept of designing a bulk material with high density of phonon scattering centers so has to reduce the lattice contribution to thermal conductivity but at the same time have minimum impact on charge carriers. This is usually achieved by utilizing interphase and grain boundaries which are localized defects to scatter phonons. The volume fraction of the grain/interphase boundaries can be control through phase modification and microstructure design. This thesis is centered on Bi-Sb-Te systems which are the present room temperature state of the earth thermoelectric material. The investigation revolves around developing a new kind of

microstructure in the well-studied Bi-Sb-Te system that shows tremendous potential as a means to reduce lattice contribution to thermal conductivity. The idea of having both p and n-type thermoelectric material preferably from the same material was also a motivation in our investigation. The thesis is divided into six chapters.

The first chapter introduces the concept of thermoelectricity i.e. the direct conversion of thermal energy into electricity. The physics involved and contribution of individual to the science of thermoelectricity were enumerated. Efficiency, optimization and material selection for better thermoelectric performance were briefly enumerated. Prospective materials that are currently being investigated for better thermoelectric properties were also mentioned. The structure of the Bi-Sb-Te system which is the focus of this thesis is present in this chapter including doping effect on the thermoelectric performance of the system as well as the various methods present been employed to improve the thermoelectric properties of the system. Finally the chapter enumerates the scope and object of the present thesis.

The different experimental procedures adopted in the present thesis are discussed in chapter 2. The details of different processing routes followed to synthesize flame-melted ingots, flame-melted + low temperature milled (cryo milling) + spark plasma sintering (SPS) alloy and flame-melted + melt spinning + spark plasma sintering (SPS) alloy, are discussed followed by the various structural and functional characterization techniques. The unique advantage of the spark plasma sintering techniques over the conventional sintering method was talked out in detail. The structural characterizations performed on the synthesized alloys include XRD, SEM and while the functional characterizations comprised of Hall measurement, Seebeck coefficient, electrical resistivity and thermal conductivity measurements.

Thermoelectric properties of selected composition of Bi-Sb-Te synthesized via flame-melting are presented in chapter 3. Detail study of four analyzed compositions namely $\text{Bi}_{24}\text{Sb}_{20}\text{Te}_{56}$, $\text{Bi}_{20}\text{Sb}_{12}\text{Te}_{69}$, $\text{Bi}_{16}\text{Sb}_5\text{Te}_{79}$ and $\text{Bi}_{29}\text{Sb}_{11}\text{Te}_{60}$ resulted in four unique microstructure and different volume fraction of primary and secondary phases. The resultant morphologies of the microstructure were observed to have influence the thermoelectric behavior corresponding to each composition. The sole influence of anti-structural defects on the conductivity type and the role of microstructure morphologies and length scale were understood in this chapter. Samples with segregated Te and a solid solution BiSbTe_3 (eutectic morphology) form an n-type thermoelectric material while samples with only solid solution BiSbTe_3 forms a p-type thermoelectric material. Pair of n-type and p-type material was obtained without the introduction of external dopant. The pair shows good compatibility factors suitable for thermoelectric device.

In chapter 4, the thermoelectric properties of four selected composition of Bi-Sb-Te synthesized via low temperature milling plus spark plasma sintering is addressed. The analyzed compositions are as follows $\text{Bi}_{24}\text{Sb}_{20}\text{Te}_{56}$, $\text{Bi}_{18}\text{Sb}_{11}\text{Te}_{71}$, $\text{Bi}_{17}\text{Sb}_6\text{Te}_{77}$, and $\text{Bi}_{28}\text{Sb}_{15}\text{Te}_{57}$ respectively. The effect of low temperature milling combine with the prospect of minimum grain growth of spark plasma sintering on the thermoelectric properties of the selected compositions were determined. Samples with eutectic morphology which would otherwise scatter charge carriers were observed to have the highest carrier mobility as a result of high volume fraction of Te phase which serves as a donor injecting excess electrons into the system. The impact of small grain size was observed on the transport properties of the sample $\text{Bi}_{28}\text{Sb}_{15}\text{Te}_{57}$ with the highest electrical resistivity, the best Seebeck coefficient and the lowest thermal conductivity. Pair of n-type and p-type material was obtained without the introduction of external doping elements. The pair shows good compatibility factor suitable for segmented thermoelectric device.

Chapter 5 narrates the thermoelectric properties of four compositions namely $\text{Bi}_{30}\text{Sb}_{13}\text{Te}_{58}$, $\text{Bi}_{23}\text{Sb}_{13}\text{Te}_{65}$, $\text{Bi}_{18}\text{Sb}_5\text{Te}_{77}$ and $\text{Bi}_{23}\text{Sb}_{20}\text{Te}_{58}$ subjected to melt spinning plus spark plasma sintering. High cooling rate obtained during melt spinning process was observed in this chapter to cause a shift of composition which resulted in a microstructure morphology with eutectic colonies that is predominantly Te rich. These Te rich colonies in the sample $\text{Bi}_{30}\text{Sb}_{13}\text{Te}_{58}$ was observed to change the conductivity type of the sample from an otherwise p-type to n-type while also aiding bipolar conduction which was detrimental to the overall thermoelectric performance of the alloy. Segregated Te in the form of eutectic morphology helps to inject excess electron into the bulk of the sample $\text{Bi}_{23}\text{Sb}_{13}\text{Te}_{65}$ and $\text{Bi}_{18}\text{Sb}_5\text{Te}_{77}$ hereby increases the observed electrical conductivity which by virtue of the microstructure morphology is expected to be low. As a result of the processing routes, all four compositions in this chapter shown-type conductivity.

Chapter 6 presents the summary of the important conclusions drawn from this work.