CHAPTER 1

INTRODUCTION

"Energy cannot be created nor destroyed"

----- Albert Einstein

Energy is one of the most important building blocks in determining the economic development all over the world as well as acts as a key factor in human development. At present, the energy demand is accelerating at an alarming rate due to the human dependence on advanced technologies, which are the sources of energy consumption and cannot be ignored. Moreover, global energy consumption increases due to the rapid industrial development, advanced technologies, and growing human population all over the world. Energy crisis is likely to lead the future supply-demand mismatches and increase the attention of scientific community to look for alternative energies to fulfil the needs of the future. To overcome this crisis one must come across towards the new energy systems as well as alternative energies such as solar energy, wind energy, biomass energy, geothermal energy, nuclear energy and thermoelectrics (TE), etc [1].

1.1 Thermoelectric materials:

Thermoelectric materials are the materials to convert heat into electricity [2]. Thermoelectric devices have unique features such as no moving parts, no refrigerants, no lubricants, no seals, quieter operation, no emissions, and no vibrations etc. Thus, it can be used more efficiently in the present system without changing the present technology [3]. In most of the systems, 60-65 % energy is unutilized as a waste heat which can be converted into useful electrical energy by thermoelectric materials (TE material) available in the nature as shown in Fig. 1.1. The energy conversion depends on the efficiency of thermoelectric material.
Figure 1.1: Pi chart of loss of energy in several industries as waste heat, which can be utilized using thermoelectric modules.

The efficiency of thermoelectric material can be judged by quantity called figure of merit (ZT) [4]:

\[ ZT = \left( \frac{S^2\sigma}{k} \right) T \]  \hspace{1cm} (1.1)

Where, 
- S: Thermo power or seebeck coefficient in (\(\mu V/K\))
- \(\sigma\): Electrical conductivity (ohm\(^{-1}\)cm\(^{-1}\))
- k: Thermal conductivity (Wm\(^{-1}\)K\(^{-1}\))
- T: Absolute temperature (K)
These thermoelectric materials can be utilized for power generation as well as refrigeration. Thermoelectric device can be fabricated by combination of p type and n type thermoelectric materials as shown in Fig. 1.2 (a), (b) for power generation as well as refrigeration respectively [5].

![Diagram](image)

**Figure 1.2:** (a) Schematic of conversion of waste heat into electricity (Seebeck effect) and (b) electricity to cooling (Peltier effect).

The mechanism for the conversion of heat into electricity from TE device can be explained by two methods Seebeck effect and Peltier effect. Combination of p-type and n-type materials in TE device provides the two types of mobile charge carriers (electrons or holes). These mobile charge carriers (electrons or holes) at the hot side of the material have more thermal energy than carriers at the cold side which causes a net diffusion of mobile carriers to the cold side. The diffusion of mobile carriers to the cold side results in the inhomogeneous charge distribution and forms an electric field, which opposes the further
diffusion. If the system is connected to a circuit, the electrochemical potential will drive a current, which results in thermoelectric power generation as shown in Fig. 1.2 (a). Vice versa of conversion of waste heat to electricity is the conversion of electricity to cooling and show the peltier effect as displayed in Fig. 1.2 (b) [5].

Thermoelectric efficiency strongly depends on working temperature. Thermoelectric materials are classified on the basis of temperature ranges due to their temperature dependent characteristics as shown in Fig. 1.3 [6]. The well known thermoelectric materials are BiSb, Bi$_2$Te$_3$, PbTe and Si$_x$Ge$_{(1-x)}$. The most commonly used thermoelectric materials are Bi$_2$Te$_3$, PbTe and Si$_x$Ge$_{(1-x)}$ having Figure of merit 0.9 at 300K, 0.8 at 770K and 0.9 at 1000K respectively.

![Figure 1.3: Different thermoelectric materials having ZT in different temperature ranges [6].](image)

Thermoelectric device efficiency is limited to few applications due to its low Figure of merit (ZT). To utilize TE device in various applications, it must have high efficiency, which directly related to ZT. The development and identification of high performance TE materials
have proven to be extremely challenging task. Unfortunately, it is noteworthy to mention that nature does not provide us materials with high electrical conductivity ($\sigma$) and low thermal conductivity ($k$) simultaneously in bulk materials. Thus, optimization of electrical and thermal conductivity suggests that neither metals nor insulators are good thermoelectric materials instead, semiconductors and semimetals can be good thermoelectric materials.

The quantities thermo power ($S$), electrical conductivity ($\sigma$) and thermal conductivity ($k$) for conventional bulk crystalline system (3D) are interrelated in such a way that it is very difficult to control independently to increase $ZT$. This is because, increase in $S$ (lowering carrier concentration) usually resulting in decrease in $\sigma$, and increase in $\sigma$ produces increase in electronic contribution to $k$ according to Widemann Franz law. To enhance the figure of merit, selecting a good thermoelectric material is a big challenging task, because conductors have high electrical conductivity as well as high lattice conductivity and vice-versa in case of insulators. Semimetals and semiconductors play an important role to get high electrical conductivity and low thermal conductivity and also by controlling the carrier concentration, $ZT$ can be optimized to get high peak at different temperatures as shown in Fig. 1.4.

![Figure 1.4: Optimization of figure of merit (ZT) to get high efficiency for different materials.](image)
Nanostructured material:

Nano materials have been classified into three type of structures 2D, 1D and 0D which are named as thin film, nano wire and quantum dot respectively. In bulk systems, due to the interdependency of all three parameters $\sigma$, $S$, $k$ to each other improvement in ZT was difficult. Thus, a new approach for improvement in ZT has been explored using nano dimensional systems where the new variable of length scale allows new opportunities to vary $S$, $\sigma$, and $k$ independently [7-10]. Nanomaterials have many interfaces, which scatter phonons more effectively than electrons to achieve very low thermal conductivity. The size of nanostructures can be engineered in such a way that reduction in thermal conductivity ($\kappa$) is more than reduction in electrical conductivity ($\sigma$).

Density of states can be varied with the variation of dimension of a system from bulk (3D) to quantum well (2D) to quantum wire (1D) to quantum dot (0D) as shown in Fig. 1.5. Tuning of density of states due to quantum confinement effects also leads to the enhancement of thermo power, which in turn results in enhancement of the figure of merit. Mott drives the formalism, which shows the relationship of thermo power with density of states. The power dependence on density of states can be given by Mott relation (Eq. 1.2) [11]:

$$ S = \frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln \sigma}{\partial E} \right|_{E=E_f} \tag{1.2} $$

Where, $k_B$ - Boltzmann constant

$E$ - Particle energy

$T$ - Temperature

Electrical conductivity $\sigma = N e \mu$, $N$ is carrier density, $\mu$ is the mobility. This equation (1.2) suggests that increase in density of states leads to the enhancement in thermo power.
Figure I.5: Density of states of (a) bulk (3D), (b) thin film (2D), (c) nano wire (1D) and (d) quantum dot (0D).

To compete the demand of new generation of advanced technology, thin films play an important role. Thin films have applications in electronic components, electronic displays, magnetic films for data storage, optical data storage devices, optical coatings, antistatic coatings and hard surface coatings. Thin films have also applications in energy related fields such as in thermoelectric, solar energy conversion, Hydrogen conversion, CO₂ conversion to Hydrocarbon fuels, bioactive and biocompatible coatings etc [12].

At present, in this thesis, focus is on synthesis of PbTe thin film due to its unique features. PbTe is an efficient thermoelectric material, which can be tuned as n-type & p-type with Pb excess & Te excess respectively without any external doping. It is a unique feature in these thermoelectric materials. PbTe can be used in several applications in various fields.
such as IR detectors, photo detectors and in thermoelectric device between temperature ranges (500-900 K). It has applications in industrial wastage, microelectronics, vehicles, and spacecrafts, etc.

1.2 Lead Telluride (PbTe):

Lead Telluride (PbTe) is a semiconductor with face centred cubic (fcc) structure, high melting point (924 °C), direct band gap (~ 0.32 eV) at room temperature, low vapour pressure, good chemical stability, good chemical strength. The crystal structure of PbTe is shown in Fig.1.6, which is cubic in structure having lattice constant 6.50 Å. The phase diagram of PbTe is shown in Fig. 1.7, reveals that Te excess results in p-type PbTe and Pb excess results in n-type PbTe.

![Figure 1.6: Crystal structure of PbTe shows face centred cubic (fcc) structure with lattice parameters 6.50 Å [13], figure shows Pb atoms occupying the cation sites and Te forming the anionic lattice.](image)

8
Figure 1.7: Phase diagram of PbTe, shows PbTe formation at 924 °C with 50 at.% of Te, Pb, and p-type, n-type PbTe results with Te excess, Pb excess respectively [14].

Lead telluride alloy is one of the first thermoelectric materials, commercialized for power generators. In the early 1950’s-1960’s, both United States and the Soviet Union, started work on PbTe and similar alloys for thermoelectric applications [15]. NASA also used PbTe for Apollo missions and Viking 2 mission to Mars. In 1960’s Fritts’s [16] reported that the figure of merit (ZT) in bulk PbTe systems is \( \sim 0.7 \). Over the three decades (1950-1990), the thermoelectric industry grown slowly and has negligible industrial interest due to the low TE device efficiency.
1.2.1 Literature review of PbTe:

Several research groups have reported figure of merit (ZT) in bulk thermoelectric systems by doping different materials as well as in different concentrations such as Na, Tl, Se, Sb, etc. PbTe doped with Se, PbTe$_{1-x}$Se$_x$ has shown high figure of merit ZT $\sim$ 1.8 at $\sim$ 850 K [17], ZT $\sim$ 1.5 is reported for 2 % Tl doped PbTe [11]. 1-2 % Na doped PbTe showed enhancement in ZT $\sim$ 1.4 at 750 K [18]. Controlled doping of I in PbTe, PbTe$_{1-x}$I$_x$ has given ZT $\sim$ 1.4 [19].

High ZT values of 1.7–1.8 is obtained in the PbTe nano composite with coherent nano-inclusions AgSbTe$_2$ [20], NaSbTe$_2$ [21], SrTe [22], etc. while only 1.4–1.5 is obtained in PbTe nano composite with incoherent nano-inclusions Sb [23], Ag$_2$Te [24], etc. Thermoelectric properties has been enhanced, ZT $\sim$ 1.2 at 773 K with Sb doping in PbTeS i.e. sample Sb$_{0.004}$Pb$_{0.996}$Te$_{0.88}$S$_{0.12}$ [25]. Thermo power has been tuned with the size of PbTe nano crystal, which enhances with decrease in the crystal size [26].

Synthesis of PbTe with different nanostructures has also been done using different methods, which may be useful for various applications. PbTe nanorods [27], micro towers [27], nano needles [28], nano boxes [29], Hierarchical binary-phased PbTe/PbSe microporities [30], nano flower [31] and crystal nano sheets [32] have been synthesised by different methods such as thermal evaporation, aqueous chemical route, solvothermal method, hydrothermal and lithography technique. These structures have given unique properties such as enhancement in blue shift [28] and in thermoelectric properties [30-32].

1.2.1.1 PbTe thin film (2D):

Synthesise of PbTe thin film has been reported by different methods such as thermal evaporation [33-40], flash evaporation method [41], electrodeposition method [42], e$^-$ beam evaporation [43], radio frequency (R.F.) sputtering [44-45], molecular beam epitaxy [46-51]
and rapid injection solution phase synthesis route [52], etc. Specially, these films show much affect in the industrial applications such as in the field of IR detectors [36, 53-55], photoelectric devices [36, 43, 52, 56-58]. Besides this, PbTe thin films have also applications in thermoelectrics. Till the date, only some research groups have focused towards the synthesis of PbTe thin films for thermoelectric applications which are discussed below:

PbTe single crystal shows electrical conductivity ~ 10-100 (ohm cm)^{-1} for carrier concentration ~ 10^{18} /cm^{3}, and for mobility of p-type carriers 860 cm^{2}/volt-sec [59]. Electrical resistivity of the air exposed PbTe thin film synthesised by vacuum deposition reported to be 2 to 3 orders of magnitude higher than that of the as-grown (unexposed) PbTe thin films (few kΩ) [35]. Sn doped PbTe (Pb_{0.8}Sn_{0.2}Te) thin films synthesised by flash evaporation method and they have shown the reciprocal thickness dependence with resistivity (varies from 0.05 – 0.3 (Ωcm)^{-1}) [41]. Since, PbTe is prone to oxidation, Roghacheva et al., has coated protective layer of EuS on thermally evaporated PbTe thin film (~ 200 nm) to avoid oxidation and reported the thermo power ~ 200 μV/K [37]. PbTe superlattice (SL) structures 55 Å period PbTe/PbTe_{0.75}Se_{0.25} has been synthesised by thermal evaporation and have shown ZT ~ 1.75 at 425 K [38]. PbTe with 2 at.% excess lead with film thickness (d= 5-200 nm) synthesised by thermal evaporation shows that an inversion of the dominant charge carrier sign from n to p takes place at d~40 nm [39]. Thin film of p-Pb_{0.925}Yb_{0.075}Te:Te and n-Pb_{0.925}Yb_{0.075}Te has been reported by thermal evaporation method and used as thermoelectric generator [40]. PbI_{2} doped PbTe films (film thickness 2-3 μm) synthesised by R.F. sputtering and to understand potential barrier scattering thermoelectric properties have been shown [45].

These tireless efforts by all over the world's research groups suggest that there is still need to look for new ideas and concepts. Review of the literature indicates that there is a lot of scope to fabricate high quality PbTe thin films with enhanced figure of merit, which
requires mainly the tuning of composition of material, formation of nanostructures as well as to tailor the material properties without use of external doping. On the other hand, it has also been seen from the literature that PbTe thin films easily get oxidized, which affects the inherent properties of material. In the view of these salient points, it is a very great challenge for scientific community to explore for an alternative technique, which can fulfil all above requirements. Ion beam technique is one of the potential tools for synthesis of PbTe thin film, which can be helpful to understand phase formation and growth of nanostructures in the film.

Ion beam mixing of bilayer samples by ion irradiation can fulfil all the requirements such as the formation of high quality PbTe thin film without affecting its intrinsic properties, which will be helpful to study the properties of PbTe. It can form the stochiometric PbTe and also able to tune the p-type (excess Te) and n-type (excess Pb) PbTe. This can be achieved by precise control over the film thickness, high atomic density of Te can make p-type PbTe and high atomic density of Pb can make n-type PbTe as well as optimization of ion beam parameters such as fluence. It is a novel route to synthesize the material, doping the material, modify the material properties and nanostructuring with fine tune in shape and size of nanostructures. Ion irradiation also helps in oxygen desorption, which is already presented in the film [60]. This technique can also helps to modify the thermoelectric properties [61-63] with the reduction of thermal conductivity, enhancement in thermo power and electrical conductivity, which may be due to possibility of defects, vacancies, density of states enhancement and phonon scattering etc.

After the literature review of PbTe and role of ion beam using the range of energies low (100 keV's) to high (100 MeV’s) for formation of required phase, nanostructures with different sizes, shapes, to understand the basic mechanism of ion solid interaction and to control over the material properties, following motivation is given.
1.3 Motivation:

In the light of fore mentioned reasons, fabrication of PbTe (2D) thermoelectric material and tuning of its properties are very important. In the present study, focus is to synthesis of stoichiometric and formation of different types of nanostructures in PbTe thin film as follows:

- Synthesis and characterization of PbTe thin film by thermal evaporation technique and comparative study of the temperature dependent power factor of thin films of pristine, ion irradiated (high energy) and annealed samples.

- Synthesis and characterization of stoichiometric PbTe thin film using high energy (100 MeV) ion beam mixing of bilayer Te/Pb (~ 20 nm each).

- Synthesis and characterization of stoichiometric PbTe thin film using low energy (90 keV Ar, 140 keV Kr) ion beam mixing of bilayer Te/Pb (~ 20 nm each).
References:


27. V. Tamilselvan, R. Rakesh Kumar and K. Narasimha Rao, Mat Lett. 96 (2013) 162.

