Synthesis and Thermoelectric Study of Series of Bismuth Tellurium selenide mixed metal Chalcogenide Thin Films by APT

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Abstract: Thermoelectric study of bismuth tellurium selenide $Bi_2(Te_{1-x}Se_x)_3$ thin films were done. They are deposited by Arrested Precipitation Technique (APT). These thin films were prepared using a complexing agent triethanolamine (TEA) and a reducing agent sodium sulphite to avoid hydroxide formation of bismuth precursor $Bi\ (NO_3)_3$ in aqueous medium to favor the reaction with Te^{2-} and Se^{2-}chalcogen ions. The preparative conditions such as pH, concentration of precursors, temperature, rate of agitation and time were finalized at initial stages of deposition. As deposited films were annealed at constant temperature (373K) in muffle furnace and then characterized for optostructural, morphological, thermoelectric and figure of merit (ZT). The results demonstrate that the $Bi_2(Te_{1-x}Se_x)_3$ thin films prepared by APT shows band gap in the range 0.98eV to 1.63eV. X-Ray Diffraction (XRD) pattern, Scanning Electron Microscopy (SEM) images reveals that $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide films are of nanocrystalline nature and have rhombohedral structure and better morphology. EDAX study shows good stoichiometry. Electrical and TEP study shows $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide thin films are semiconducting having p-type conduction mechanism. The figure of merit obtained ranges from 0.778 to 0.141 for F1 to F7 samples respectively.

Keywords: APT, Metal chalcogenides, X-ray diffraction, Figure of merit, Thermoelectric.

Introduction

The thermoelectric device can convert thermal energy from a temperature gradient into electric energy. When a temperature differential is established between the hot and cold ends of the semiconductor materials, a voltage is generated. The thermoelectric devices can also act as power generators. Oppositely, thermoelectric devices can convert electrical energy into a temperature gradient. Thermoelectric devices have several advantages over traditional coolers and power generators such as no moving parts, no working fluid (e.g. steam or Freon substitutes) and noiseless operation [1]. Metal chalcogenide plays important role as a thermoelectric material. Among all the chalcogens Te and Se is one of the most important chalcogen elements. The works on binary Se-alloys have already been reported [2-6]. Se-Te has been used as a base material and incorporation of Bi as a third element has been studied [7]. A large value of the thermoelectric efficiency Z of these materials is due to the high degeneracy of the energy band edges. It is necessary to increase the Seebeck coefficient or the electric conductivity in order to increase the thermoelectric efficiency. This is of particular interest for applications at room temperature. Now a day $Bi_2(Te_{1-x}Se_x)_3$ is the best performing n-type thermoelectric material [8-12]. In the present work, we have studied the structural and electrical properties of ternary $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide thin films.

1. Experimental set up for deposition of $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide thin films:-

Experimental set up for deposition of $Bi_2(Te_{1-x}Se_x)_3$ and mixed metal chalcogenide thin films is as below

a) Deposition of $Bi_2(Te_{1-x}Se_x)_3$ thin films by Arrested precipitation technique

In chapter two we discussed different techniques for deposition of the various metals, ceramic polymer and alloy thin film on variety of the substrate materials. Out of these in our research we use Arrested precipitation technique (APT) for deposition of ternary $Bi_2(Te_{1-x}Se_x)_3$ mixed metal thin films. Because a deposition technique depends upon several factors such as film thickness, surface area, nature of substrate supports application of thin film. This process is relatively slow therefore it facilities better orientation, crystallinty of thin film. Also this method is low deposition process it avoids intermetalic conversion as well as thermal expansion of substrate. APT is important not only for effectiveness in the reduction of low cost. But also for the high quality of the materials one can achieves by such method.

In the arrested precipitation method we use organic complexing agent such as EDTA, citric acid, triethanolamine, tartaric acid etc. to arrest the metal ions by forming metal ligand complex. So controlled dissociation of arrested metal ion at basic pH was takes place slowly (ion by ion). The film formation involves creation of a nucleation centres at the substrate surface followed by growth of metal chalcogenide by the ion by ion condensation of appropriate ions from solutions. Certain time this result in saturation of film growth known as terminal growth phase of thin film deposition [13-15].

b) Solutions required for preparing $Bi_2(Te_{1-x}Se_x)_3$

All chemicals used in experiment were analytical reagent (AR) grade manufactured by E-Merck and Hi-Media. These chemicals are

❖ Bismuth nitrate	$Bi(NO_3)_3.5H_2O$
❖ Anhydrous Sodium sulphite-	Na_2SO_3
❖ Selenium metal powder-	Se
❖ Tellurium metal powder-	Te
❖ Triethanolamine (TEA) -	$[N(CH_2\text{-}CH_2\text{-}OH)_3]$

➢ **Preparation of precursor solutions**

Bismuth tellurium selenide thin films have been prepared by an arrested precipitation technique by allowing the Bi-TEA complex to react with Te^{2-}, Se^{2-} ions, which are released slowly by the dissociation of Na_2TeSO_3 and Na_2SeSO_3 in alkaline medium at pH 10.5. For the experiment all solutions were prepared in double distilled water.

➢ **Bi-TEA complex**

0.05M Bismuth nitrate $[(Bi(NO_3)_3.5H_2O]$ was prepared by triturating 2.425 gm Bismuth nitrate in 20ml triethanolamine (TEA) for six hours and diluted to 100ml with distilled water

➢ **Sodium tellurium sulphite (Na_2TeSO_3) solution**

0.05M Sodium tellurosulphite solution prepared by refluxing 30gm Na_2SO_3 and 7 gm elemental tellurium metal powder in 250 ml distilled water at 100°C for 12 hours in a 250ml round bottom flask. After refluxing the solution was filtered and diluted to obtain 0.05M Na_2TeSO_3.

➢ **Sodium seleno sulphite (Na_2SeSO_3) solution** 0.05 M Sodium seleno sulphite solution prepared by refluxing 30gm Na_2SO_3 and 6 gm elemental selenium metal powder in 250 ml distilled water at 100°C for 6-7 hours in a 250 ml round bottom flask. After refluxing the solution was filtered and diluted to obtain 0.05M Na_2SeSO_3.

***c*) Deposition of $Bi_2(Te_{1-x}Se_x)_3$ thin films**

Deposition bath was prepared by addition of 20 ml 0.05M bismuth triethanol ammine complex, 0.05 M Na_2TeSO_3 (1-x) and 0.05 M Na_2SeSO_3 (x) rest is water to make 100ml by adding distilled water in 150ml beaker. Where concentration of mixed phases are varied in the ratio x=0 to1. Thoroughly cleaned glass substrate was mounted on a substrate holder. The parameters such as pH of the bath was made 10.5 ± 0.2 by addition of 1:1 ammonia solution , time (2 hours), temperature of deposition bath (55 ^{0}C) and speed of substrate rotation (45±5 rpm) were optimized. After deposition, samples were taken out, washed with distilled water and kept in dark desiccators. Remaining all mixed bismuth tellurium selenide $Bi_2(Te_{1-x}Se_x)_3$ thin films were prepared by varying concentrations of selenium and tellurium. Amount of Bi-TEA complex and its concentration were kept constant for all compositions. The concentrations of Te^{2-}, Se^{2-} were varied in a volume stoichiometric ratio so as to obtain various compositions of $Bi_2\ (Te_{1-x}Se_x)_3$ thin film. Table 1.1 shows the variations of Te^{2-}, Se^{2-} in $Bi_2(Te_{1-x}Se_x)_3$ in the film composition the samples were designated as F_1 to F_7 respectively.

Table 1.1 Composition of the sample for deposition of $Bi_2\ (Te_{1-x}Se_x)_3$ thin films

Sample No.	Composition
F_1	Bi_2Te_3
F_2	$Bi_2(Te_{0.8}Se_{0.2})_3$
F_3	$Bi_2(Te_{0.6}Se_{0.4})_3$
F_4	$Bi_2(Te_{0.5}Se_{0.5})_3$
F_5	$Bi_2(Te_{0.4}Se_{0.6})_3$
F_6	$Bi_2(Te_{0.2}Se_{0.8})_3$
F_7	Bi_2Se_3

Table 1.2. Bath composition and preparative conditions for the $Bi_2(Te_{1-x}Se_x)_3$ thin films

Film composition	Bath composition	Preparative conditions	Thickness (µm)
$Bi_2(Te_{1-x}Se_x)_3$ (F_1 to F_7)	20 ml 0.05 M Bi-TEA + 0.05 M Na_2TeSO_3 (1-x) and 0.05 M Na_2SeSO_3 (x) rest is water to make 100 ml total volume. Where concentration of mixed phases are varied in the ratio x=0 to1	pH = 10.5 ± 0.3 Temperature = 55 ± 0.5 ^{0}C Deposition time = 2 hrs Substrate rotation = 45 ± 5 rpm	Between 0.21µm to 0.71µm

At such rapid rate of reaction deposition of desired metal chalcogenide on substrate material could not be possible. Hence in order to slow down the rate of reaction Bi^{3+} ions are arrested by using suitable complexing agent. The metal complex hydrolyses slowly at basic pH to generate the positive ions (Bi^{3+}) in the solutions. Triethanolamine was used as complexing agent for bismuth (III) and antimony (III) ions. Table 1.2. shows bath composition and preparative conditions for the $Bi_2(Te_{1-x}Se_x)_3$ thin films.

d) Growth mechanism of $Bi_2(Te_{1-x}Se_x)_3$ thin film formation

The detail of nucleation and growth depends on the material being deposited and other parameters such as reaction time, temperature, complexing agent, pH, and required precursors to maintain a high simultaneous nucleation rate and good size distribution for synthesis of $Bi_2(Te_{1-x}Se_x)_3$ thin films .

In arrested precipitation technique, a complexing agent is used to bind the metallic ions to avoid the homogeneous precipitation of the corresponding compound. The formation of complex ion is essential to control the rate of reaction and to avoid the immediate precipitation of compound in the solution. The metal complex hydrolyses slowly to generate the positive ions in solution. A solution containing the metal complexes were mixed with a solution which produces negative ions by hydrolyses. When the solution is saturated, the ionic product is equal to the solubility product and when it exceeds, ions combines on the substrate to form the nuclei. It is known that entire process passes through nucleation phase, growth phase and a terminal phase [17]. The presence of the surface of a substrate introduces a degree of homogeneity that facilitates nucleation in film growth processes. Therefore, the surface of the substrate can be considered a catalyst activating the nucleation. Once nucleation has begun on a substrate, it generally becomes easier for the film to grow, since deposition usually occurs more easily on the nucleated surface than on the clean surface. Either homogeneous or heterogeneous deposition can occur. The homogeneous process is the faster one, resulting in the adsorption of powdery particles on the substrate due to the bulk precipitation. So, the formation of metal complex is essential to minimise the homogeneous process. In the heterogeneous process, the preferential adsorption of Bi^{3+}, Te^{2-} and Se^{2-} ions will take place, leading to the uniform nucleation and growth of the thin film. Addition of NH_4OH increases the OH^- ion concentration in the solution and thereby favours the hydrolysis of the chalcogen precursor.

APT is suitable for the deposition of $Bi_2 (Te_{1-x} Se_x)_3$ mixed type thin films. According to Ostwald ripening law if metal ions in solution are arrested using polydentate complexing agent like TEA, the rate of reaction between metal ions and chalcogenide ions can be well controlled to get desired quality of metal chalcogenide thin films. In the present investigation, we have slightly modified the chemical deposition method using polydentate chelating agent, triethanolamine $[N(CH_2\text{-}CH_2\text{-}OH)_3]$ as a complexing agent to arrest Bi^{3+} ions. The stability constant indicate strong affinity of the organic complexing agent TEA towards Bi^{3+} ions and it's tendency to keep the Bi^{3+} ion arrested in a solution even in alkaline pH range where the metal hydroxide formation is possible. Concentration of precursors also shows strong influence on the growth of $Bi_2 (Te_{1-x}Se_x)_3$ thin films. In the present investigation ionic species of $Bi^{3+,}$ Te^{2-} and Se^{2-} are produced as per the following reaction equilibria [18, 19].

During the deposition process $Bi^{3+,}$ Te^{2-} and Se^{2-} ions are slowly releases in the solution in an aqueous alkaline deposition bath. The formation of $Bi_2(Te_{1-x} Se_x)_3$ thin films occurs when ionic product of $Bi^{3+,}$ Te^{2-}, and Se^{2-} exceeds the solubility product of $Bi_2(Te_{1-x} Se_x)_3$ .Overall growth mechanism of the mixed composites of Bismuth tellurium selenide are summarized as follows.

$$(NH_4)_3[Bi_2 N (CH_2\text{-}CH_2\text{-}O)_3] + 6H_2O \rightarrow Bi^{3+} + 3NH_4OH + 3OH^- + 2[N(CH_2\text{-}CH_2\text{-}OH)_3] \quad (1)$$

$$Na_2TeSO_3 + OH^- \rightarrow Na_2SO_4 + HTe^- \quad (2)$$

$$HTe^- + OH^- \rightarrow H_2O + Te^{2-} \quad (3)$$

$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$ (4)

$HSe^- + OH^- \rightarrow H_2O + Se^{2-}$ (5)

The reactions given in equation (1) to (5) shows that the Bi^{3+}, Te^{2-} and Se^{2-} are condenses ion by ion basis on the glass substrate at pH 10.5 and 55°C temperature as follows:

$Bi^{3+} + nNa_2TeSO_3 + nNa_2SeSO_3 \rightarrow Bi_2(Te_{1-x}Se_x)_3 + nNa_2SO_4 + n(TEA)$ (6)

TEA is stable throughout the deposition period and temperature. Finally, the deposited $Bi_2(Te_{1-x}Se_x)_3$ films prepared by arrested precipitation technique are found to be uniform and well adherent to the substrate. Chemical reaction is followed by annealing in order to form stable single phase solid solutions. After annealing, specimens are cut into pieces of different size for measurement purposes and to enhance the mechanical and thermoelectric properties.

2. *Thermoelectric study $Bi_2(Te_{1-x}Se_x)_3$ thin film*

a) Electrical conductivity

Electrical conductivity of a material is the reciprocal of the electrical resistivity**.** The electrical conductivity of the films was studied by using two point D. C. probe method. As the contact resistance of the films is very low (10^{-3} ohm) compared to film resistance, the two probe method is accurate and hence used for electrical conductance measurements.

Electrical conductivity measurement was made in the temperature range 300 K to 500 K at constant voltage (5 volt). The temperature dependence of electrical conductivity of the semiconducting thin films is given by equation;

$$\sigma = \sigma_0 \exp\left(-\frac{Ea}{kT}\right) \qquad (7)$$

where k is Boltzmann constant, σ_0 is the temperature dependent part of the conductivity and E_a is activation energy. The variation of $\ln \sigma$ with 1000 / T in the temperature range 300 to 500 K for as deposited and annealed samples were shown in Figure 1.1 a and Figure 1.2 b. From graph it reveals that electrical conductivity increases after annealing for two hours at 100 ^{0}C. The measurement shows an increase in electrical conductivity of the materials with increase in temperature indicating all the films are semiconducting nature. For mixed composites $Bi_2(Te_{1-x}Se_x)_3$ thin films, the electrical conductivities lies between those of Bi_2Te_3 and Bi_2Se_3 for as deposited and annealed samples. From the slope of linear plots, activation energies were calculated for two temperature region. The activation energies for low temperature region and in high temperature region were represented in Table 1.3

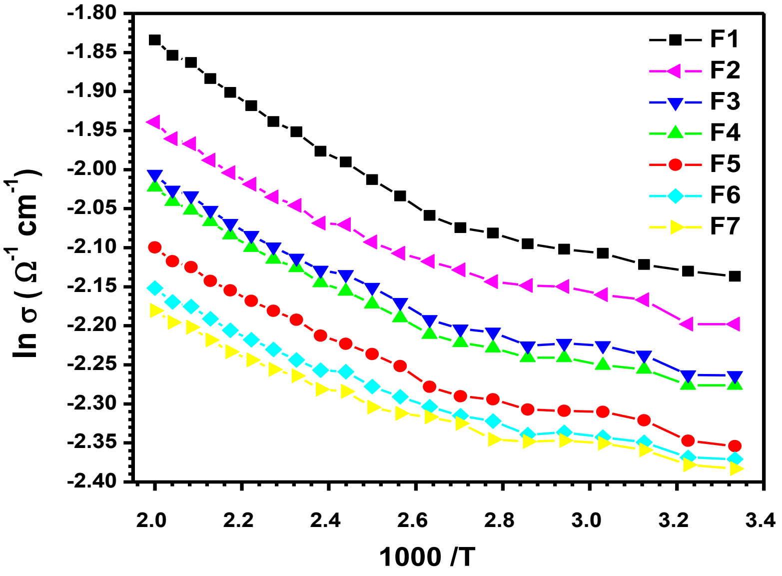

Figure 1.1 a) The variation of $\ln \sigma$ with 1000 / T for as deposited F_1 to F_7 sample

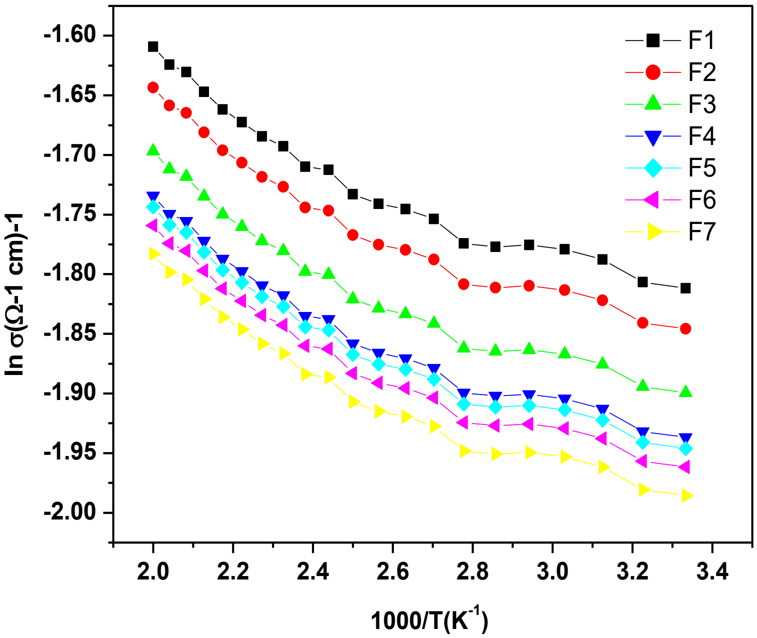

Figure 1.1 b) The variation of ln □ with 1000/T samples for annealed F_1 to F_7 samples

Table 1.3 Observed variation of activation energy (ΔE) for $Bi_2(Te_{1-x}Se_x)_3$ thin films

Film Composition	**Before Annealing**		**After Annealing**	
	High temperature region ΔE (eV)	**Low temperature region ΔE (eV)**	**High temperature region ΔE (eV)**	**Low temperature region ΔE (eV)**
F_1 : Bi_2Te_3	0.2983	0.0803	0.43362	0.1606
F_2 : $Bi_2(Te_{0.8}Se_{0.2})_3$	0.300	0.0812	0.43848	0.1624
F_3 : $Bi_2(Te_{0.6}Se_{0.4})_3$	0.305	0.0854	0.46116	0.1708
F_4 : $Bi_2(Te_{0.5}Se_{0.5})_3$	0.3161	0.1117	0.60318	0.2234
F_5 : $Bi_2(Te_{0.6}Se_{0.4})_3$	0.3191	0.1178	0.63612	0.2356
F_6 : $Bi_2(Te_{0.2}Se_{0.8})_3$	0.3457	0.1033	0.55782	0.2066
F_7 : Bi_2Se_3	0.426	0.1095	0.5913	0.219

b) **Thermal electrical power (TEP) measurement**

The Seebeck coefficient of a material depends on the electronic band structure of the material. Typically metals have a low Seebeck coefficient because most have half-filled bands. The positive and negative charge carriers are present in approximately equal quantity. The induced thermoelectric voltage thus cancels each other's contributions. However, semimetals and semiconductors can be alloyed and doped to increase either the positive or the negative charge, thus increasing the Seebeck coefficient of the material. The sign of the thermo power can determine which charged carriers dominate the electric transport in both metals and semiconductors.

The two common types of Seebeck coefficient measurement are the DC and AC methods. In our laboratory we use fixed point DC method. It consists of simultaneous measurement of temperature and the voltage difference between the cold region and the hot region of the material. Thermocouples are connected to the cold and hot regions, to measure the temperature, while the voltage difference between the corresponding leads of the thermocouples is measured and recorded. These thermocouples are stationary during the data acquisition. The Seebeck coefficient of the material is calculated by equation;

$$S = \Delta V / \Delta T \qquad (8)$$

where, S is the Seebeck coefficient, ΔV is the voltage difference between the copper wire of the thermocouple and the ΔT is the temperature difference between the thermocouples. The experimental calculation of the Seebeck coefficient has to account for the Seebeck voltage generated in the copper wires. The mean temperature was measured with a Meco 801 digital multimeter while the differential thermal gradient and thermoelectric voltage were measured with digital Testronix - 8 microvoltmeter.

The temperature dependence thermo emf for all these films are shown in figure at 300 to 500 K. Thermoelectric measurements were made using the integral method in which one end of the film was heated and other kept at a constant low temperature and developed thermal electromotive force was measured with respect to the temperature gradient.

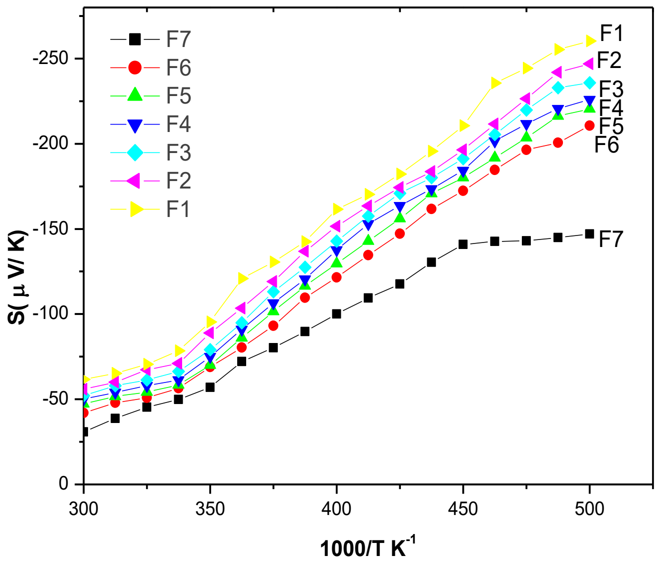

Figure 1.2 a) Variation of thermo emf with temperature for as eposited F_1 to F_7 samples

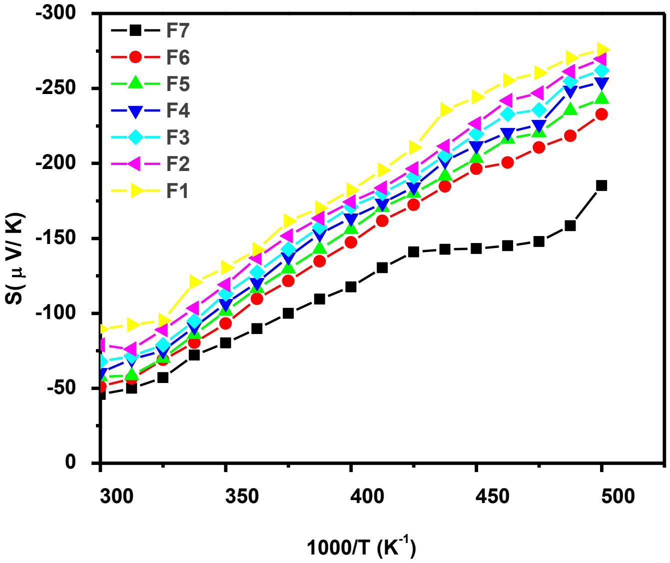

Figure 1.2 b) Variation of thermo-emf with temperature for annealed F1 to F_7 samples

In the present work all the samples shows –ve polarity of the generated voltage. This confirms n-type conduction of the samples [53, 54]. Figure 1.2 a) and 1.2 b) shows Seebeck coefficients. Before annealing it found to be -61.59 to -30.79 μV/K. Whereas after annealing Seebeck coefficient increases from - 45.90 to - 89.59 μV/K [55, 56].

c) Thermal conductivity

The thermal conductivity (κ) is a sum of the electronic (κ el), lattice (κ ph) and ambipolar (κ am) components given by equation;

$$k = kel + kph + kam \qquad (9)$$

where κ el is directly proportional to the Lorentz constant. Electronic thermal conductivity (κ el) is related to electrical conductivity (σ) by the Wiedemann - Fraz law equation;

$$kel = L\sigma T \qquad (10)$$

where L is the Lorentz number is equal to 2.45 x 10^{-8} WΩ/K and T is the absolute temperature. The temperature dependence of thermal electrical conductivity (Kel) was used to calculate the figure of merit and represented in Table 1.3 and 1.4 accordingly.

The thermal conductivity of thin films is lower than those of bulk sample [57]. The thermal conductivity inversely varies with thickness indicates additional scattering from interface/grain boundary in thin films [58, 59]. As a result, the thermal conductivity measurement was performed at room temperature 300 K shows decrease in thermal conductivities from 0.340 to 0.474 W/mK for F_1 to F_7 sample before annealing and 0.370 to 0.492 W/mK for F_1 to F_7 sample after annealing respectively [60]. Figure 1.3 shows, chemical composition dependence thermal conductivity.

- **Thermoelectric performance (ZT)**

Doped semiconductors are most effective materials, because they have high electrical conductivity and low thermal conductivity as compare to pure metal and glass. Pure metals have very high electrical conductivity but very low thermal conductivity. Opposite phenomenon is observed in case of glasses. The glasses have low thermal conductivity but also very low electrical conductivity.

Bi_2Te_3 materials are most effective thermoelectric materials at room temperature. Thermoelectric materials are capable of converting heat directly into electricity, According Seebeck when temperature gradient is applied on the material then at the hot end of the material; thermally electrons are more than the cold end. Concentration gradient is created. If such material is connected in open circuit then due to development of electrochemical potential diffusion of charge carriers towards the cold side is stopped to attain the equilibrium. This electrochemical potential is nothing but Seebeck voltage.

Peltier coefficient is a material dependent parameter. This parameter describes how much thermal energy is carried per charge carrier. If heat is absorbed the thermoelectric materials are acting as a refrigerator. $Bi_2(Te_{1-x}Se_x)_3$ is semiconductor used in electric industry. It also strongly used as a thermoelectric material because of its good electrical properties and low thermal conductivity.

Materials which are able to efficiency generate power or refrigerate are known as thermoelectric materials. Depending upon properties of material we would like able to determine whether a given material will be a good thermoelectric material or not. Material should have high electrical conductivity, low thermal conductivity and high Seebeck coefficient. Dimensionless figure of merit can be calculated by equation 11.

$$ZT = \frac{S^2}{\rho . k} \times T \qquad (11)$$

Where, S is the Seebeck coefficient which is measure of the average electron energy in a material, ρ is the resistivity, k is the thermal conductivity and T is the absolute temperature at which the properties are measured [61,62].

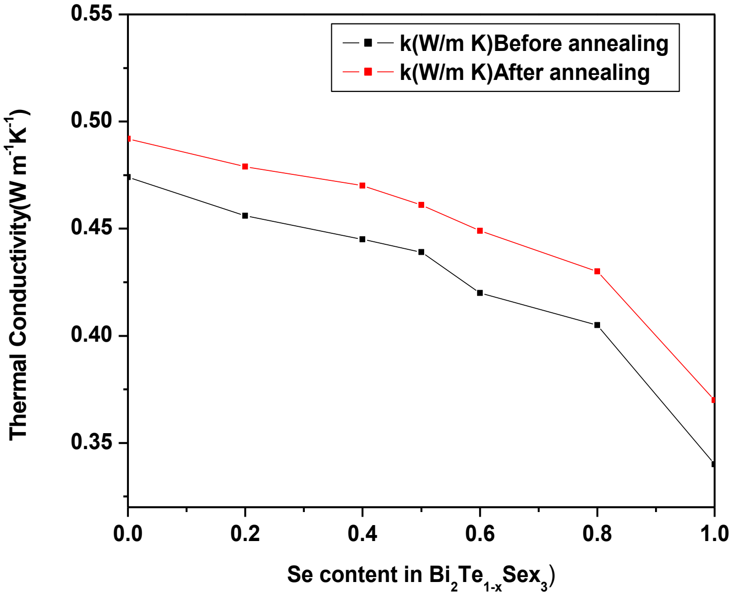

Figure 1.3 Variation of thermal conductivity with Se content in $Bi_2(Te_{1-x}Se_x)_3$ (*Note*: x varied between 0 to1 values)

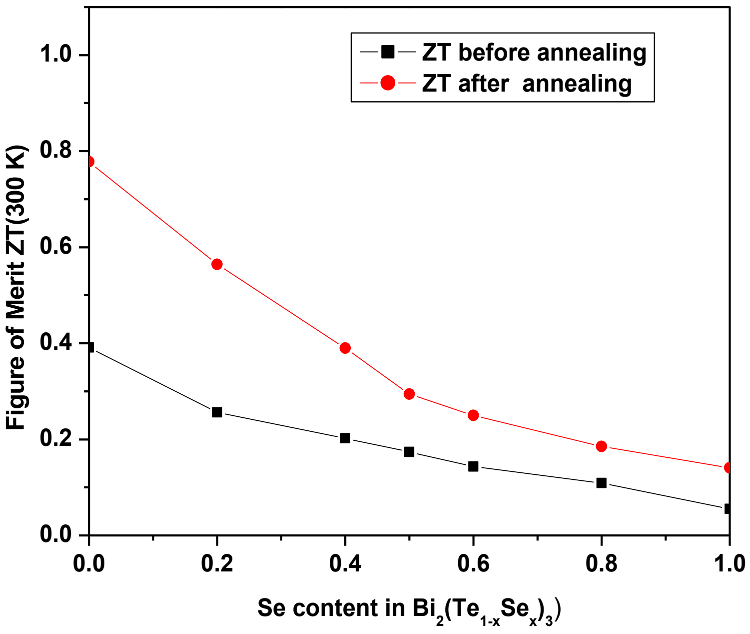

Figure 1.4 Variation of Figure of merit with Se content in $Bi_2(Te_{1-x}Se_x)_3$

(*Note*: x varied between 0 to1 values)

The quality of thermoelectric materials was described by dimensionless figure of merit, ZT. Figure 1.4 shows the temperature dependence of ZT value. While the value of ZT materials was about 0.77 to 0.141 after annealing for 2 hours at 100ºC [63].The room temperature ZT values are shown in Table 1.4. Due to continued increase of the Seebeck coefficient in all samples, the power factor (S^2/ρ) and thermoelectric performance (ZT) increase substantially at higher temperatures [64].

The calculated values for the figure of merit for Bi_2Te_3 thin films are some what higher (0.77) than those reported for films deposited by co-sputtering (0.31), by electrochemical deposition (0.07) and are nearly close to those reported for films deposited by metal-organic chemical vapour deposition is 0.98, by flash evaporation is 0.53. This anomalous behavior may be due to novel spherical nano-structural nature of Bi_2Te_3 thin films. These results suggest that, the prepared Bi_2Te_3 materials are promising for thermoelectric refrigeration, cooler etc. [65].

Table 1.4 Thermoelectric properties of annealed F_1 to F_7 samples of $Bi_2 (Te_{1-x}Se_x)$ thin films

Film Composition	S (μV/K)	ρ (μΩm)	κ (W/m K)	PF(mWK-2m-1)	ZTat300K (μW/cmK^2)
F_1: Bi_2Te_3	**-89.59**	**6.78**	**0.370**	**0.914**	**0.778**
F_2:$Bi_2(Te_{0.8}Se_{0.2})_3$	-78.79	7.67	0.430	0.809	0.564
F_3:$Bi_2(Te_{0.6}Se_{0.4})_3$	-67.90	7.90	0.449	0.583	0.3899
F_4:$Bi_2(Te_{0.5}Se_{0.5})_3$	-60.55	8.10	0.461	0.452	0.294
F_5:$Bi_2(Te_{0.4}Se_{0.6})_3$	-57.75	8.50	0.470	0.392	0.250
F_6:$Bi_2(Te_{0.2}Se_{0.8})_3$	-51.15	8.85	0.479	0.295	0.185
F_7:Bi_2Se_3	-45.90	9.10	0.492	0.231	0.141

d) Conclusions

The $Bi_2 (Te_{1-x} Se_x)_3$ thin films were successfully deposited by APT and characterized by optostructural, morphological and electrical studies. The UV-Vis spectrum of the films reveals that the deposited films having band gap in the range of 0.98 to 1.63 eV. The XRD pattern of the film shows rhombohedral structure. SEM and AFM micrographs show that films are compact, uniform and adherent with pin-hole-free nature. From EDAX analysis the compositions of the films are in good stoichiometric ratio. Minor deviation in composition is because of antisite effects caused due to more metallic behavior of bismuth in Te^{2-} and Se^{2-} environment. Comparison of I-V measurements of thin films without dye loaded and dye loaded of $Bi_2(Te_{1-x}Se_x)_3$, it shows that the total conversion efficiency increases for dye loaded thin film is high as compared to thin films without dye. This is attributed to the fact that the density of charge carriers increased due to maximum light absorption by dye sensitized photoelectrodes in the visible region. This application gives unique route for the development of dye sensitized ECPC cell. Electrical and TEP study shows that $Bi_2(Te_{1-x}Se_x)_3$ mixed metal chalcogenide thin films are semiconducting having n-type conduction mechanism. The highest figure of merit obtained was 0.77 for Bi_2Te_3 sample.

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