

## STRUCTURAL AND THERMOELECTRIC PROPERTIES OF THERMALLY EVAPORATED PbTe THIN FILMS

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Thin films of lead telluride (PbTe) of different thicknesses ranging between 500 Å to 2500 Å have been prepared by thermal evaporation technique onto precleaned amorphous glass substrates at room temperature. Selected virgin samples were annealed at temperature 523 K for 60 min. in vacuum ( $\approx 10^{-5}$  torr). The X-ray diffraction analysis confirmed that these annealed films are polycrystalline corresponding to the rock salt (NaCl) FCC structure. From the XRD profiles, the grain size, dislocation density, micro strain and lattice constants were calculated. Resistivity of the virgin and annealed samples was measured by four-probe technique as a function of thickness and temperature. The resistivity was measured in the temperature range of 303 K to 473 K. It was observed that for virgin samples the resistivity decreases with increasing film thickness. It shows the NTC behavior of resistivity. For the annealed PbTe films the resistivity shows dramatic change resulting in oscillatory behavior with increasing film thickness. Thermoelectric power has been measured by the integral method in the same temperature range and found to be positive indicating that the samples are p-type semiconducting materials. The existence of oscillations in the thermoelectric properties for both the virgin and annealed samples is attributed to quantum size effects.

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*Keywords:* Thermal evaporation; lead telluride; XRD, SEM, resistivity; thermoelectric power.

### 1. Introduction

The IV–VI semiconductors PbS, PbSe and PbTe with the cubic NaCl (rock salt) structure, generally known as lead salts, have been the subject of a vast amount of theoretical and experimental work during the past decades, motivated not only by their technological applications, but also by their unusual physical properties. The unusual characteristics of lead salts such as high carrier mobilities, high dielectric constants and narrow band gaps make them unique among polar compounds and have important applications in many fields, such as infra-red detectors, light-emitting devices and more recently as infra red laser in fiber optics and thermoelectric devices [1–4]. Studies about heterostructures, films, quantum wires and quantum dots or wells of lead salts and their applications have caused much attention in the recent past [5–9]. The lead chalcogenides exhibit very interesting photoelectric, photoconducting, thermoelectric, thermoresistive, optical and semiconducting properties. L.Kungumadevi et al studied the ac conductivity and dielectric properties of thermally evaporated PbTe thin films [10]. The transport properties of co-evaporated PbTe thin films were studied by U.P. Khairnar et al [11]. M. M. El - Ocker et al studied the effect of film thickness on the optical properties of thermally evaporated PbTe thin films [12]. PbTe is an intermediate thermoelectric power generator and its maximum operating temperature is 900 K. PbTe has high melting point, good chemical stability, low vapor pressure and good chemical strength in addition to high figure of merit ( $Z$ ) [13]. Mandale A.B. [14] has studied resistivity, Hall

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constant, mobility, carrier density and thermoelectric power of vacuum deposited lead telluride films formed at room temperature and evaluated the effective hole mass from the observed thermoelectric power and correlated with transport properties. Abd El-Ati [15] has studied the electrical conductivity of PbTe thin films in which a transition of conductivity from n- type to p-type was observed. E.I.Rogacheva et al [16] reported oscillatory dependences of the transport properties on the layer thickness  $d$  in  $n$ -PbTe, which were attributed to quantum size effects due to electron confinement in the IV-VI quantum wells.

In the present work the resistivity, thermoelectric power and structural information of thermally evaporated PbTe films on glass substrates have been studied and an attempt is made to explain their dependence on the thickness and annealing of the PbTe thin films.

## **2. Experimental details**

### **2.1. Deposition of PbTe films**

Using PbTe powder (Sigma-Aldrich 99.99+ % purity) the films of various thicknesses were deposited onto unheated well cleaned glass substrates by thermal evaporation in vacuum

( $\approx 10^{-5}$  Torr) using molybdenum boat as a source. All samples of different thicknesses were deposited under almost the same environment and conditions. The rate of deposition and thickness of the films were roughly estimated by using quartz crystal thickness monitor model no. DTM-101 provided by HINDHIVAC. The film thicknesses were confirmed by using weight - difference method with the help of digital balance (DENOVER-Germany, Model: TB-214). The deposition rate was maintained 5–10 Å /sec constant throughout the sample preparations. The source to substrate distance was kept constant (14 cm) and the alumel-chromel thermocouple placed in contact with the substrates revealed that the substrate temperature remains practically constant (at  $\approx 305$  K) during the deposition. Deposited samples were kept under vacuum over night. The selected PbTe thin film samples of thicknesses 500 Å to 2500 Å were annealed at 523 K for 1 hr in vacuum ( $\approx 10^{-5}$  torr).

### **2.2. Characterization**

The X-ray diffraction (XRD) patterns of annealed PbTe samples were recorded by an X-ray diffractometer (model D-8 Advance, Bruker axs) with  $\text{CuK}\alpha$  radiation (1.5406Å). The surface morphology of PbTe films was investigated by scanning electron microscopy (SEM) using model JEOL-JSM-6360 A (Japan).

### **2.3 Resistivity and TEP measurements**

Resistivity of the samples was measured by four-probe by “Scientific Equipment and Services, Roorkee”. The thermoelectric power (TEP) has been measured by the integral method [11]. The set up used for this measurement is provided by “Pushpa Scientific Co., Hyderabad”. The set up is such that one end of the film can be connected to a heater attachment and the other end to a massive copper block in order to ensure a constant temperature. It was found that the cold end temperature was maintained at room temperature ( $\sim 303$ K) within  $\pm 1$ K. The temperature of other end could be varied from 303 to 473K. The temperature of both the ends was measured using copper-constantan thermocouple fixed right on to the film. The thermo emf (electromotive force) developed across the film was measured with respect to copper, as a function of hot-end temperature using high impedance digital micro voltmeter model No. DMV-001 provided by “Scientific Equipment Roorkee”. For the resistivity and TEP measurements both the virgin as well as annealed PbTe samples were used.

### 3. Results and discussion

#### 3.1 Structural analysis

The X-ray diffraction patterns of vacuum evaporated PbTe thin films of five different thicknesses ranging from 500 Å to 2500 Å annealed at 523 K for 1 hr in vacuum ( $\approx 10^{-5}$  torr) are shown in Fig.1

The presence of sharp peaks in the diffractogram suggests the polycrystalline nature of the film. The observed 'd' spacing and hkl planes (Table 1) are in good agreement with the JCPDS X-ray file data (card number 38-1435) of cubic PbTe and earlier reports [10,11,15] conforming the rock salt (NaCl) FCC structure of the PbTe film. From the XRD profiles, the grain size, dislocation density, micro strain and lattice constant were calculated [10]. The degree of structural order of crystalline PbTe films improves with an increase in film thickness. All PbTe films are essentially of the same crystalline single phase state except for a difference in crystallite size.

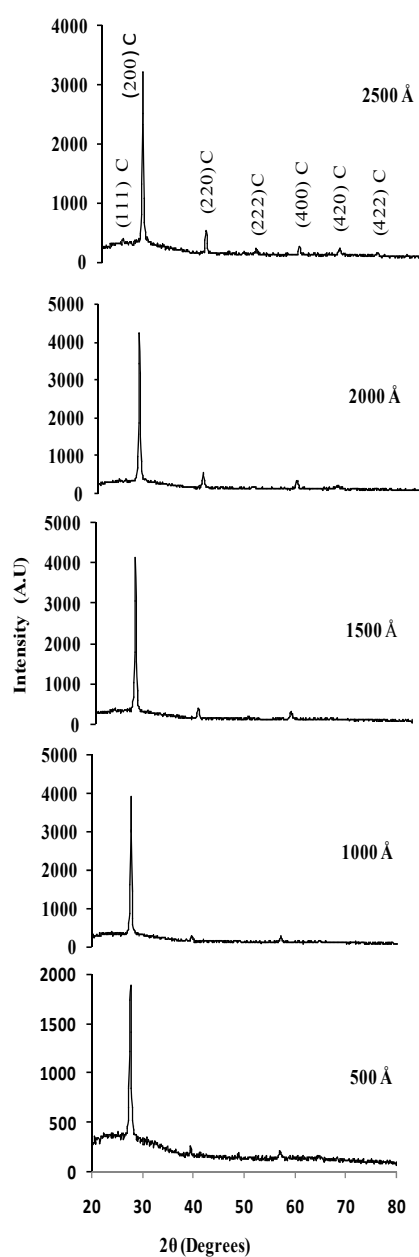


Fig.1 X-ray diffraction patterns of PbTe thin films annealed at 523 K for 1 hr in vacuum ( $\approx 10^{-5}$  torr)

It is observed that the diffraction intensity for (200) C orientation increases with increase in film thickness of up to 2000 Å due to the growth of the materials incorporated in the diffraction process. These samples also shows lower intensity peaks for (220), (222),(400),(420),(422) cubic phase. The degree of such a preferred orientation was found to increase with film thickness. But for the film thickness of 2500Å, well defined peaks for (111), (220), (222),(400),(420),(422) cubic phase are seen at the cost of the diffraction intensity for (200) C orientation. The comparison of standard (card number 38-1435) and observed XRD data for the PbTe thin films of thickness 500 Å to 2500 Å annealed in vacuum ( $\approx 10^{-5}$  Torr) is presented in Table 1

**Table 1**

Comparison of standard and observed XRD data of PbTe thin films annealed at 523 K for 60 min. in vacuum ( $\approx 10^{-5}$  torr) .

Standard						Observed									
2θ °	d (Å)	Int.	h	k	l	500 Å		1000 Å		1500 Å		2000 Å		2500 Å	
						2θ °	d (Å)	2θ °	d (Å)	2θ °	d (Å)	2θ °	d (Å)	2θ °	d (Å)
23.824	3.732	8	1	1	1	...	...	...	...	...	...	...	...	24	3.705
27.571	3.233	100	2	0	0	27.6	3.229	27.6	3.229	27.6	3.229	27.6	3.229	27.6	3.229
39.410	2.285	75	2	2	0	39.4	2.285	39.6	2.274	39.5	2.280	39.5	2.280	39.5	2.280
48.780	1.865	23	2	2	2	48.9	1.861	...	...	48.9	1.861	48.9	1.861	48.9	1.861
56.971	1.615	17	4	0	0	57	1.614	57	1.614	57	1.614	57.1	1.612	57	1.614
64.441	1.445	27	4	2	0	...	...	64.7	1.440	64.6	1.442	64.5	1.444	64.5	1.444
71.491	1.319	18	4	2	2	...	...	...	...	...	...	...	...	71.7	1.315

The lattice parameter ‘a’ has been evaluated from the relation

$$a = d [h^2 + k^2 + l^2]^{1/2} \quad (1)$$

where ‘d’ is the atomic spacing value and h, k, and l are the Miller indices.

The grain or crystallite size was determined by using Scherrer formula:

$$\text{Grain size } (D) = K \lambda / \beta \cos \theta \quad (2)$$

where the constant  $K$  is a shape factor usually  $\approx 0.94$  for cubic structure,  $\lambda$  is the wavelength of the X-ray (1.5406Å),  $\theta$  is the Bragg’s angle and  $\beta$  is the corrected FWHM.

The strain ( $\epsilon$ ) was calculated by the formula:

$$\epsilon = \beta \cos \theta / 4 \quad (3)$$

The dislocation density ( $\delta$ ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula

$$\delta = 1/D^2 \quad (4)$$

The grain size(D), strain ( $\epsilon$ ), dislocation density( $\delta$ ) and lattice constant ( $a$ ) for the annealed PbTe samples of thickness 500 Å to 2500 Å along (200) cubic phase have been calculated using above formulae and the values are given in the Table 2.

Table 2. Calculated structural parameters for the (200) cubic phase of PbTe thin films annealed at 523 K for Hour in vacuum ( $\approx 10^{-5}$  torr).

Thickness (Å)	$2\theta$ (°)	FWHM (°) ( $\beta$ )	Grain size (D) (nm)	Strain ( $\epsilon \times 10^{-4}$ ) (lines <sup>-2</sup> m <sup>-4</sup> )	Dislocation density ( $\delta \times 10^{13}$ ) (lines/m <sup>2</sup> )	Lattice constant(a) (Å)
500	27.6	0.36	24	15.13	174.62	6.46
1000	27.6	0.32	27	13.62	141.45	6.46
1500	27.6	0.29	30	12.10	111.77	6.46
2000	27.6	0.28	31	11.86	107.36	6.46
2500	27.6	0.26	33	11.02	92.57	6.46

The computed lattice constant 'a' is in good agreement with the JCPDS (38-1435) value 6.459 Å. There is an increase in crystallite or grain size (D) and decrease in strain as well as dislocation density with the increase in the film thickness. Thickness effect on structural parameters indicates that the degrees of preferred orientation along with the other micro structural features are more effective.

The Full Width at Half Maximum (FWHM) was found to decrease remarkably with film thickness. Such a decrease reflects the decrease in the concentration of lattice imperfection due to a decrease in the internal micro strain within the films and / or an increase in the crystallite size. When film thickness increases the grain size increases because larger grains begin to form on the surface of smaller grains. The effect of thickness as observed is that crystallite size increases and improves the structure of the film.

It is observed that the crystallite size increases but the dislocation density decreases with increase of film thickness. Same effect was observed by L.Kungumadevi et al [10] for the increase in annealing temperature of the PbTe thin films. Since the dislocation density and strain are the manifestation of dislocation network in the films, the decrease in the strain and dislocation density indicates the formation of higher quality films at higher film thickness. A stress is also developed in the film due to the lattice misfit. However, the stress has two components: thermal stress arising from the difference of expansion coefficient of the film and substrate and internal stress due to the accumulating effect of the crystallographic flaws that are built into the film during deposition. The average stresses of the deposited films are found to be compressional in nature. The compressive stress is due to the grain boundary effect, which is predominant in polycrystalline film.

### 3.2 SEM analysis

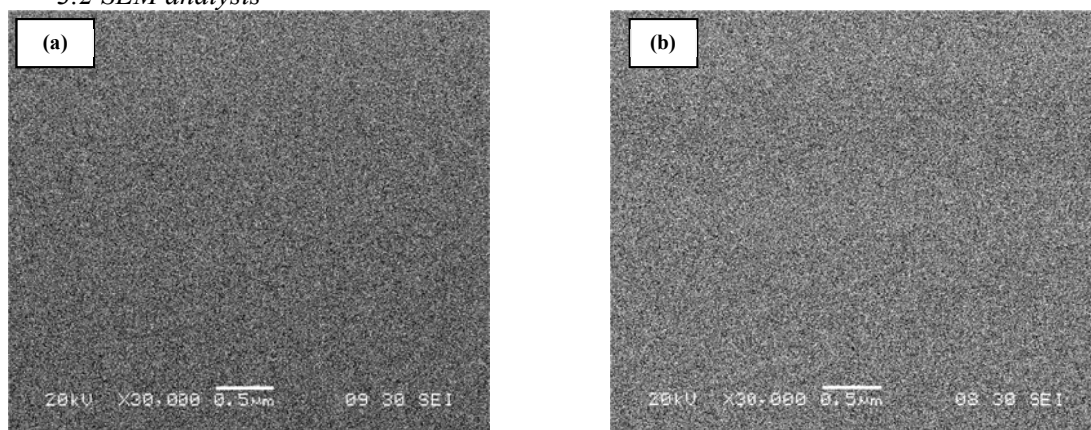


Fig.2 SEM images of thermally evaporated PbTe thin films of thicknesses (a) 2000 Å and (b) 2500 Å annealed at 250 °C for 1 hour.

Fig.2(a) and (b) shows the SEM images of thermally evaporated PbTe thin films of thicknesses 2000 Å and 2500 Å annealed at 523 K for 1 hour. For both the thicknesses, the SEM micrographs are analyzed at a resolution of 0.5  $\mu\text{m}$  with 30000 X magnification. The grains are found to be thickly packed with less inter grain spacing. This results in better crystallinity of the films. The crystallites with dimensions of the order of 30 to 40 nm are seen on the film surface which is in good agreement with the grain size determined from measured XRD data of both the films. The SEM micrograph indicates the smooth and homogeneous surface. This may be due to the highly preferred orientation of the films in the (200) plane.

### 3.3 Resistivity analysis

#### Resistivity-Temperature dependence:

Fig.3 (a) and (b) shows the variation of resistivity as a function of temperature [ $1 + \text{Log } \rho$  against  $1/T$ ] for virgin and annealed PbTe thin films respectively, indicating that all the film samples of virgin and annealed PbTe thin films of thicknesses 500Å to 2500Å have negative temperature coefficients of resistivity, which suggested their semiconducting nature [11]. These graphs shows linear variation in the temperature range 303-473K for both the cases. But for the annealed samples the curves are highly linear than that for the virgin samples.

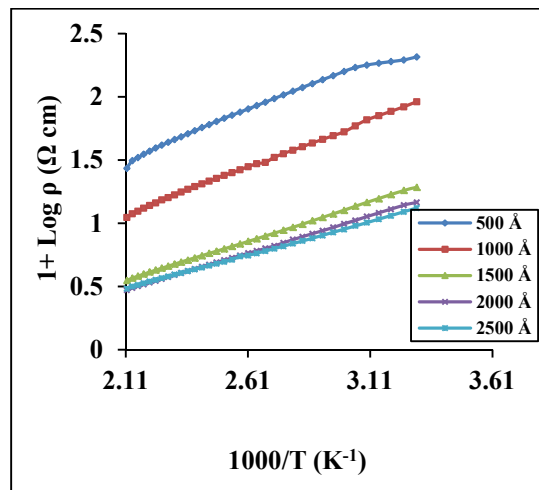


Fig.3 (a) Variation of  $\text{Log } \rho$  Vs reciprocal of temperature for various film thicknesses for virgin PbTe thin films.

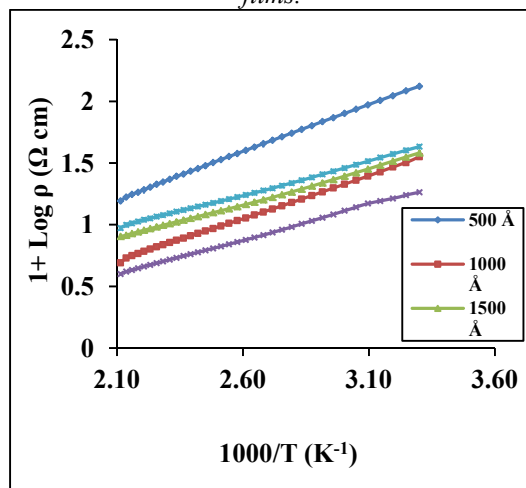


Fig.3 (b) Variation of  $\text{Log } \rho$  Vs reciprocal of temperature for various thicknesses of annealed PbTe thin film

*Resistivity - thickness dependence:*

The variation of the electrical resistivity  $\rho$  with film thickness at temperature 473 K for virgin and annealed PbTe films is shown in Fig. 4 (a) and (b) respectively.

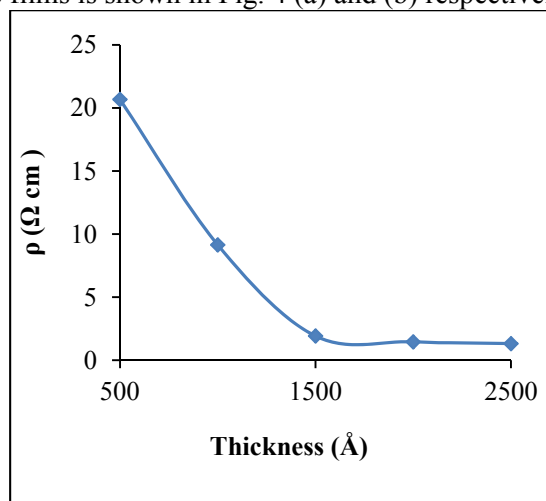


Fig.4 (a) Effect of film thickness on the electrical resistivity  $\rho$  of virgin PbTe thin films at 473 K.

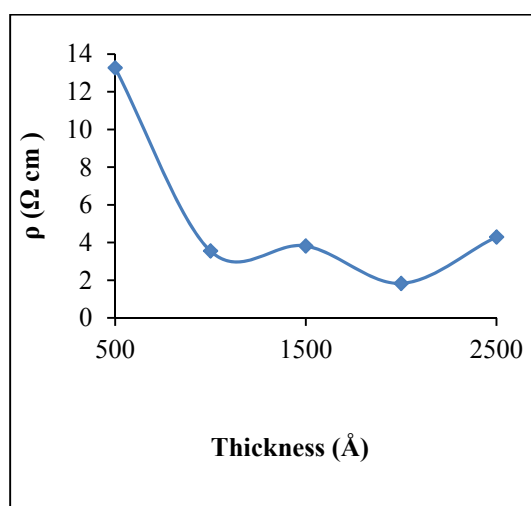


Fig.4 (b) Effect of film thickness on the electrical resistivity  $\rho$  of annealed PbTe thin films at 473 K.

From Fig.4 (a) it is observed for virgin samples that the resistivity decreases sharply with increasing film thickness up to 1500 Å and then it slows down for higher thicknesses. This means that for higher film thicknesses the conductivity increases. The high resistivity of thin films with small thicknesses is attributed to the existence of an island structure which contains many defect sites. These islands increase in area with the increase of the film thickness leading to the formation of a continuous film. This suggests that the defect density is much smaller for films deposited with larger thickness. As a result, the electrical resistivity decreases with rising film thickness. Thus for the virgin films the increase of the film thickness decreases the empty channels between the isolated islands of PbTe leading to creation of continuous film structure caused the increase of the charge carriers through the film. The decrease of the resistivity as the film thickness increase is similar to previous work [15].

But for the annealed PbTe films the resistivity shows dramatic change in its behavior with increasing film thickness as shown in Fig.3 (b) and Fig.4 (b). It shows oscillatory behavior with increasing film thickness almost for the total temperature range 303-473K. For lower film thickness of 500 Å the resistivity value obtained is maximum which afterwards decreases sharply and then oscillates with the rise in film thickness.

### 3.4 TEP Analysis

Plots of thermo emf versus temperature difference for the virgin and annealed PbTe films of various thicknesses are displayed in Fig-5(a) and Fig-5(b) respectively. It is seen that thermo emf increases linearly with increasing temperature. The linearity in the characteristics is improved for the annealed samples.

Fig -6 (a) and (b) shows the plots of thermoelectric power (or Seebeck Coefficient) against temperature for the virgin and annealed PbTe thin films of various thicknesses. Thermo emf as well as thermoelectric power of PbTe was found to be positive for all thicknesses indicating PbTe is p-type material.

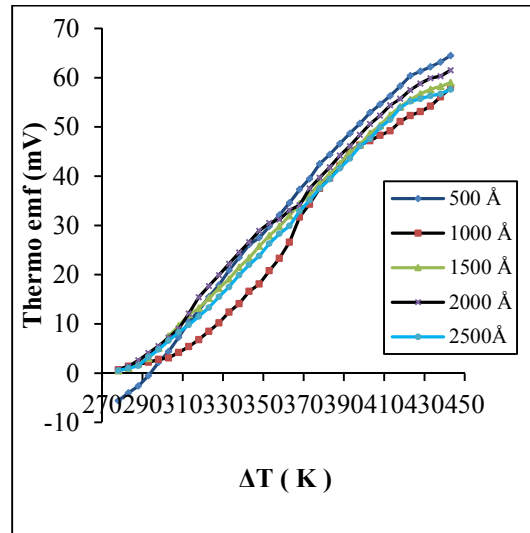


Fig.5(a) Thermoemf as a function of temperature difference for the virgin PbTe thin films.

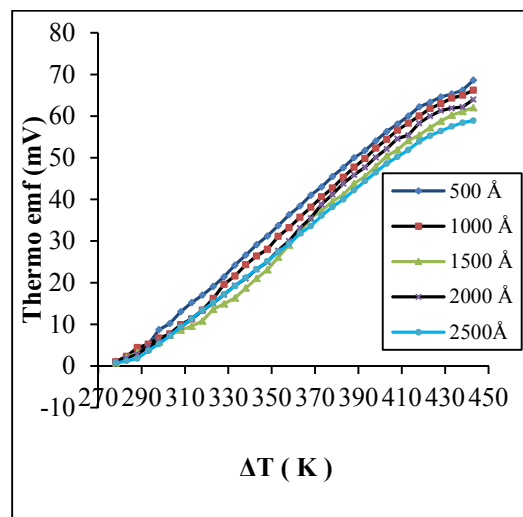


Fig.5 (b) Thermoemf as a function of temperature difference for the annealed PbTe thin films.



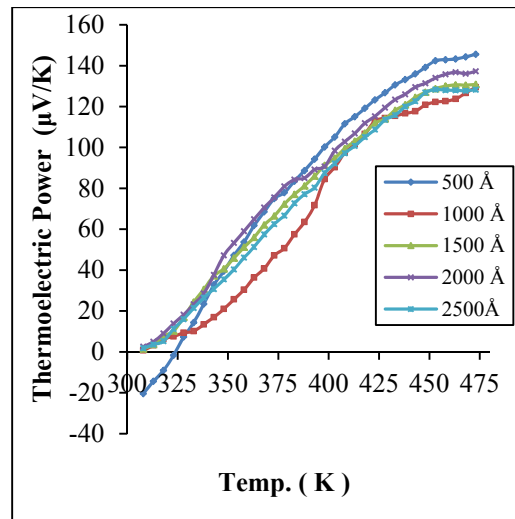


Fig.6 (a) Temperature variation of thermoelectric power for the virgin PbTe thin films.

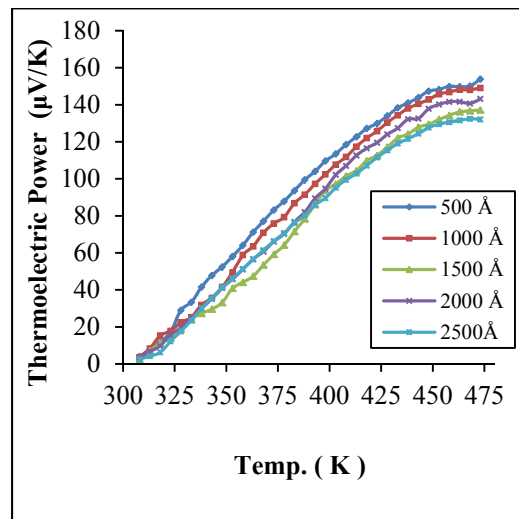


Fig.6 (b) Temperature variation of thermoelectric power for the annealed PbTe thin films.

Fig – 7 (a) and (b) shows the Seebeck coefficient dependence at 473 K on the thickness of virgin and annealed PbTe thin films respectively. For both the cases it shows the oscillatory behavior.

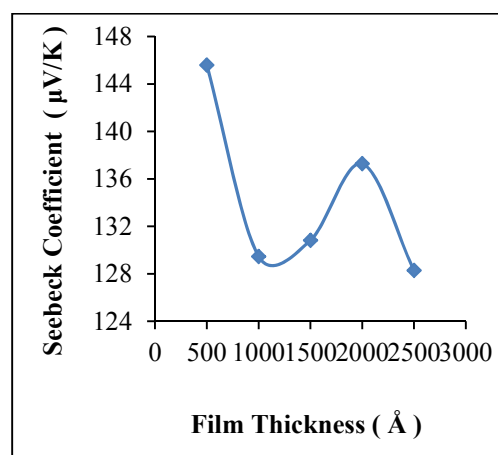


Fig.7 (a): Seebeck coefficient dependence at 473 K on thickness of virgin PbTe thin films

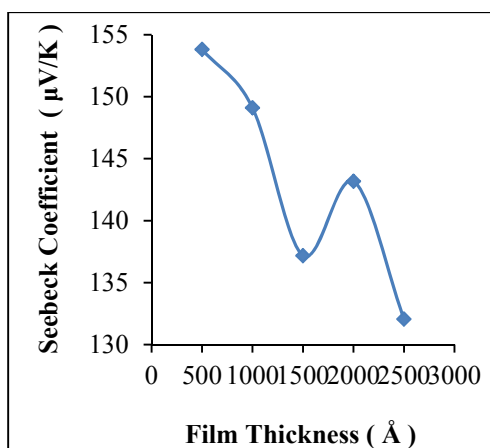


Fig.7 (b): Seebeck coefficient dependence at 473 K on thickness of annealed PbTe thin films

The existence of oscillations in the thermoelectric properties is attributed to quantum size effects. [7] This oscillatory behavior is observed for all the samples throughout the temperature range 303 K to 573 K as shown in Fig -6 (a) and (b). The value of Seebeck coefficient is increased for the annealed samples as compared with the virgin samples for all the thicknesses.

Quantization of the energy spectrum results in an oscillatory behavior of the dependence of the thermodynamic and transport properties on the film thickness [17]. It can be assumed that the oscillatory behavior of the observed thickness dependence of resistivity ( $\rho$ ) and Seebeck coefficient ( $S$ ) is due to the size quantization taking place in a PbTe film when its thickness becomes comparable to the de-Broglie wavelength [16].

#### 4. Conclusions

The X-ray diffraction patterns of vacuum evaporated PbTe thin films of five different thicknesses ranging from 500 Å to 2500 Å annealed at 523 K for 1 hr in vacuum ( $\approx 10^{-5}$  torr) shows that all XRD patterns exhibit polycrystalline nature with major diffraction peaks at  $2\theta \approx 27.6^\circ$  corresponding to the (200) plane of cubic phase. The presence of the predominant peaks corresponding to the (200) plane of cubic phase for all the films and low intensity peaks corresponding to (111), (220), (222), (400), (420), (422) planes of cubic phase confirming the rock salt (NaCl) structure of the PbTe films. Only for the higher film thickness of 2500 Å, well defined peaks for all (111), (220), (222), (400), (420), (422) cubic phases are seen. The structural parameters of the PbTe thin films such as lattice parameter ( $a$ ), crystallite size ( $D$ ), dislocation density ( $\delta$ ) and strain ( $\epsilon$ ) were calculated. The effect of thickness as observed is that crystallite size increases and improves the structure of the film. The SEM micrograph indicates the smooth and homogeneous surface. This may be due to the highly preferred orientation of the films in the (200) plane.

All the film samples of virgin PbTe thin films of thicknesses 500 Å to 2500 Å have negative temperature coefficients of resistivity, which suggested their semiconducting nature. It is observed that the resistivity decreases with increasing film thickness for the virgin samples. Thermo emf as well as thermoelectric power of PbTe was found to be positive for all thicknesses indicating PbTe is p-type material. For the annealed PbTe films the resistivity shows dramatic change resulting in oscillatory behavior with increasing film thickness. The existence of oscillations in the thermoelectric properties for both the virgin and annealed samples is attributed to quantum size effects.

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