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Thermoelectric properties of Bi_2Te_3 and Sb_2Te_3 and its bilayer thin films

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The Bi_2Te_3, Sb_2Te_3 and Bi_2Te_3-Sb_2Te_3 bilayer thin films of various thickness have been prepared using thermal evaporation at vacuum. X-ray diffraction method is used for the characterisation of the samples. Electrical studies have been carried out using the standard four probe method and then the activation energies of each film before and after annealing are obtained. Thermoelectric behaviour of each sample is also determined at various temperature regions.

Keywords: Thin films, Thermoelectric properties, Bilayer thin films

1 Introduction

The thermoelectric effect is the appearance of an electric field along a temperature gradient established in a material. The materials which convert heat flow into electrical current and vice versa are known as thermoelectric materials. Sb_2Te_3 and Bi_2Te_3 are good conventional thermoelectric materials.

These materials have the potential to act as thermoelectric devices, that directly interconvert the energy between the heat and electricity[1,2,3,4,5,6]. The performance of thermoelectric materials and devices is quantified by a dimensionless quantity called figure of merit Z, which is defined as $Z=\alpha^2\sigma/k$, where α is the seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity. Z can be increased by increasing α and σ or decreasing k. Among these properties, the reduction of thermal conductivity is thought to be the most effective approach to improve the thermoelectric performance. Though all known new electric materials are believed to have $Z \leq 1$, theoretical results of Hicks *et al.* [7] predict that thermoelectric devices fabricated as 2-D quantum well, or 1-D quantum wires could have $Z \geq 3$. A good thermoelectric material should have large seebeck coefficient (α) to produce the required voltage, low thermal conductivity (k) to keep the heat at the junction and low electrical resistivity (ρ) to minimize Joule heating[8]. V_2-VI_3 binary compounds such as Sb_2Te_3 and Bi_2Te_3 are narrow band-gap semi-conductors with the homologous layered crystal structure. Sb_2Te_3 and Bi_2Te_3 are semi-metal alloys, and have good electrical conductivity and low thermal conductivity[9,10]. They can be used for many different applications which typically fall into two general categories, power generation and cooling devices[11]. Thermoelectric power generators and coolers have many advantages over conventional refrigerators and power generators such as long life, no moving parts, no green house gases, no noise, low maintenance and high reliability[12,13]. Bi_2Te_3 is reported as N type and Sb_2Te_3 is reported as P type semiconductors. But the presence of excess tellurium may change the type. Both of them have high thermoelectric power compared to other semiconductors. They have high electrical conductivity than pure semiconductors and have low thermal conductivity. In order to improve thermoelectric properties, Sb_2Te_3 and Bi_2Te_3 can be annealed [14]. For efficient devices multiple layers of Bi_2Te_3 and Sb_2Te_3 are necessary.

In this paper, the thermoelectric properties of Bi_2Te_3, Sb_2Te_3 and its bilayer thin films prepared by evaporating solid antimony telluride and bismuth telluride have been studied.

2 Experimental Details

2.1 Thin film fabrication

All the three samples, Bi_2Te_3, Sb_2Te_3 and Bi_2Te_3-Sb_2Te_3 bilayer films are prepared by the vacuum thermal evaporation method. Deposition is done over the glass substrates. To clean the substrates, they are first washed and put in acetone and placed in ultrasonic agitator for half an hour. Substrates are taken from the acetone and dried in hot air using a heater. An oil diffusion pump backed by a rotary pump is used for attaining vacuum of the order of 10^{-6} torr. Pure antimony telluride and bismuth telluride powder are separately evaporated under a vacuum of the order of 10^{-6} torr for fabricating single layer

Sb_2Te_3 and Bi_2Te_3 thin films of thickness 1500 and 1000 Å, respectively. To prepare the bilayer film, Sb_2Te_3 is deposited on a predeposited Bi_2Te_3 film of thickness 1000 Å, up to a total thickness of 2000 Å. After several repetitions good quality thin films with high adhesion and surface features were obtained.

2.2 Film characterisation

To identify the structure of the film, X-ray diffraction method is used. X-ray diffraction pattern of Sb_2Te_3 shows three well defined peaks which imply its crystalline structure. Also in the case of Bi_2Te_3 film and the bilayer film, the X-ray diffraction analysis reveals the polycrystalline structure. Sb_2Te_3 possesses a rhombohedral structure same as that of Bi_2Te_3. Figure 1 shows XRD pattern of annealed and unannealed Sb_2Te_3 thin films. It shows three well defined peaks at the 2θ values of about 25, 30, and 40 degrees respectively. Figures 2 and 3 show the XRD patterns of unannealed and annealed Bi_2Te_3 thin films. Both have peaks at the 2θ values about 17, 24 and 27 degrees. Figures 4 and 5 are the X-ray diffraction patterns of unannealed and annealed Bi_2Te_3-Sb_2Te_3 respectively which have peaks at 28, 40, 42.5, 43.5 and 49.7 degrees.

The particle sizes have been calculated using the Scherrer formula. The average particle sizes for Sb_2Te_3 are 5.545 Å and 4.666 Å for annealed and unannealed samples, respectively. For Bi_2Te_3, it is found as 27 Å and 22.8Å for annealed and unannealed, respectively. In the case of bilayer film, for the unannealed sample, the average particle size is 21.36Å and for the annealed sample, it is found as 23.40 Å.

2.3 Electrical properties

The *dc* conductivity study is one the important study to find the behaviour of thin film materials. Conductivity studies of each sample are carried out

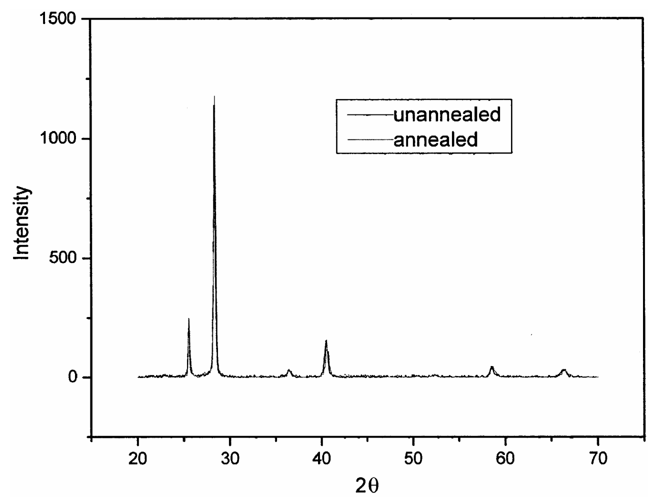

Fig. 1 — X-ray diffraction pattern of Sb_2Te_3 thin film

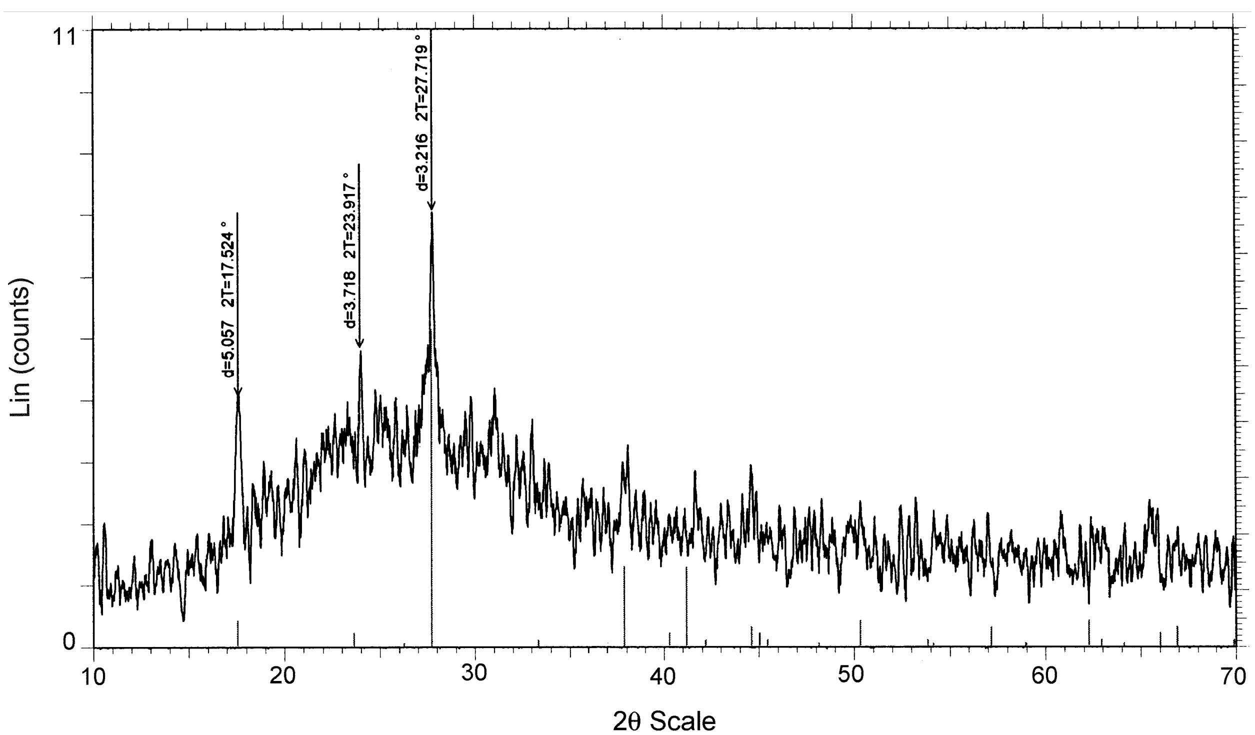

Fig. 2 — X-ray diffraction pattern of Bi_2Te_3 thin film

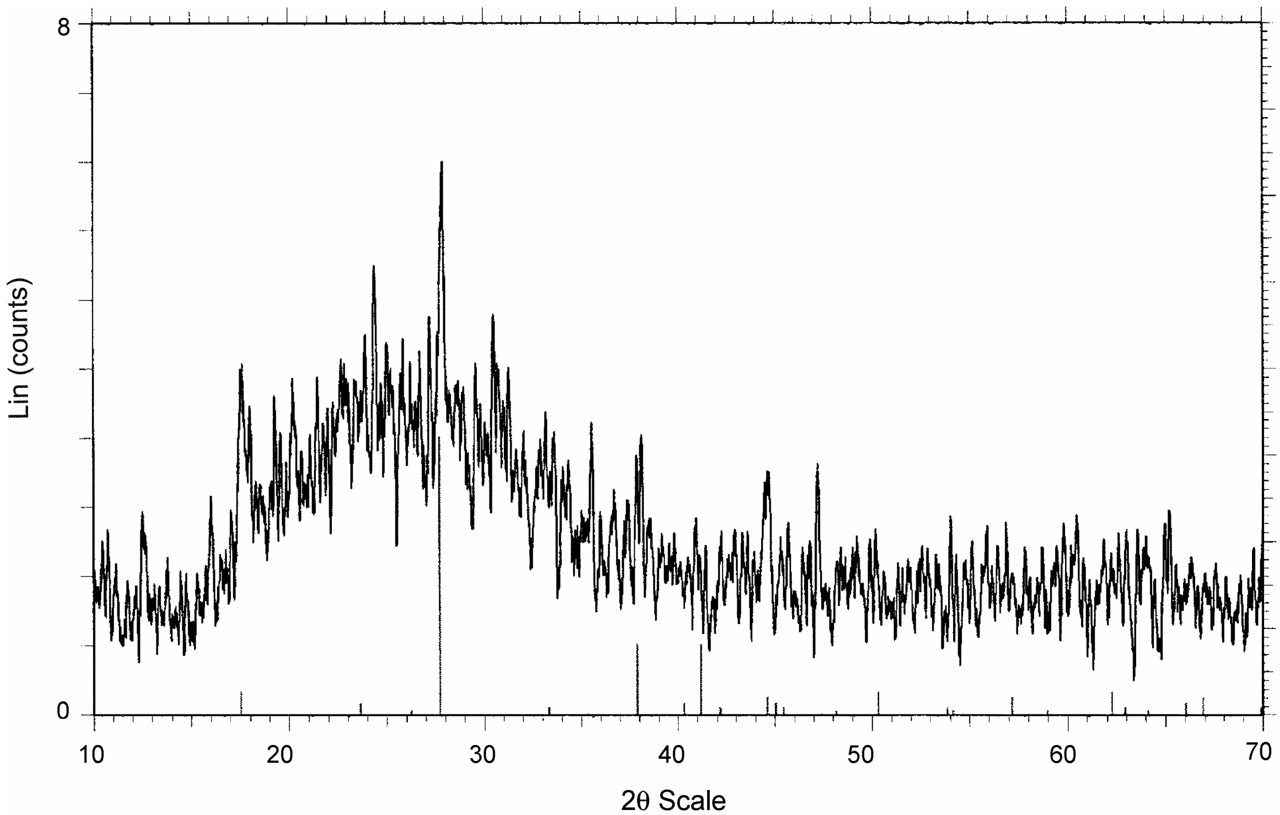

Fig. 3 — X-ray diffraction pattern of annealed Bi_2Te_3 thin film

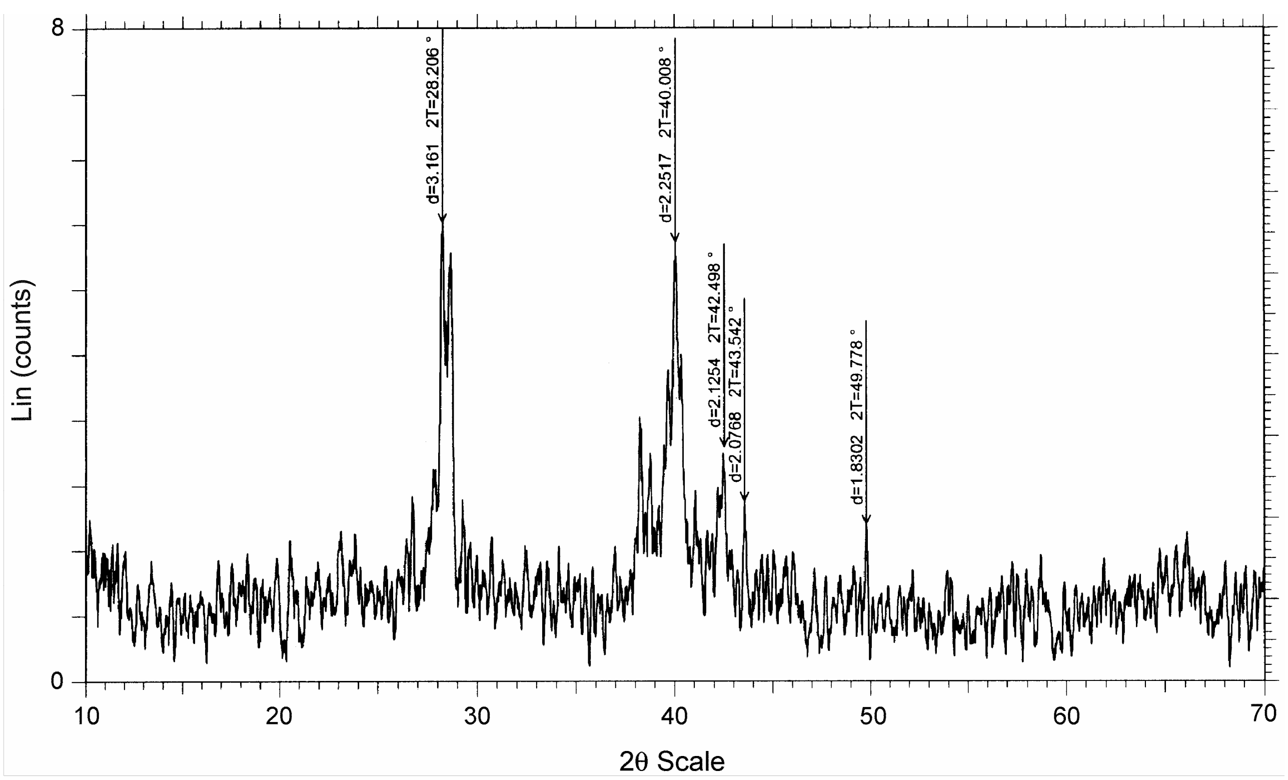

Fig. 4 — X-ray diffraction pattern of Bi_2Te_3 – Sb_2Te_3 bilayer film

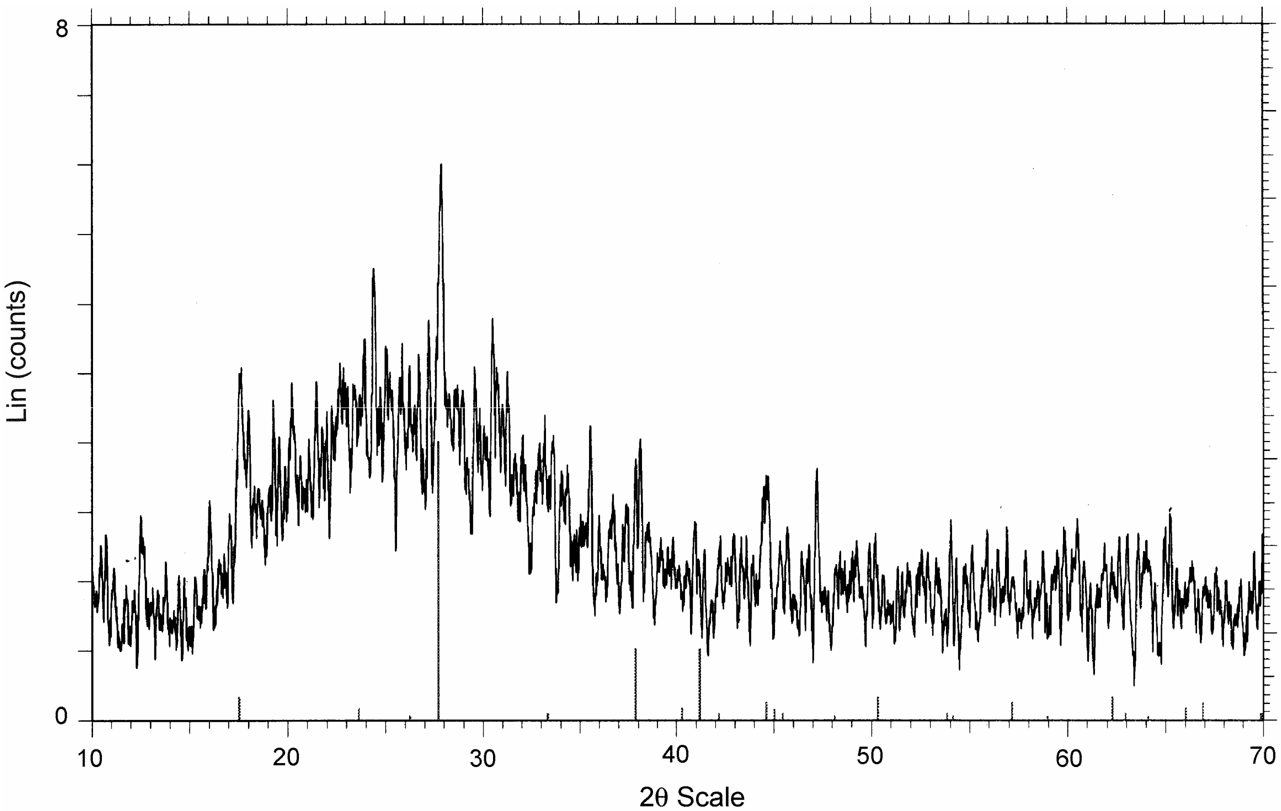

Fig. 5 — X-ray diffraction pattern of annealed Bi_2Te_3 – Sb_2Te_3 bilayer film

using standard four probe technique. Keeping the current as a constant, the voltage is measured for different temperature varying from 30 to 150°C. For each case, a graph is plotted between the inverse of temperature and log of sheet resistivity. Figures 6-8 explain the variation of sheet resistivity of Sb_2Te_3, Bi_2Te_3 and Bi_2Te_3-Sb_2Te_3 bilayer thin films respectively before and after annealing.

As the temperature increases, sheet resistivity decreases for unannealed Sb_2Te_3 film and increases for annealed Sb_2Te_3 film. From the graph, it is clear that the sheet resistivity decreases or conductivity increases with increase in temperature for unannealed Sb_2Te_3 which explains its semiconducting behaviour while annealed Sb_2Te_3 exhibits conducting behaviour, since its resistivity increases with increase in temperature. The activation energies are found as 0.007 and 0.0286 eV for the unannealed and annealed samples, respectively. In the case of Bi_2Te_3, both unannealed and annealed samples show semiconducting behaviour. The activation energies are found as 0.005 and 0.016 eV respectively. In the case of the bilayer film, the unanneled sample shows, semiconducting behaviour with an activation energy of 0.054 eV while the annealed sample shows

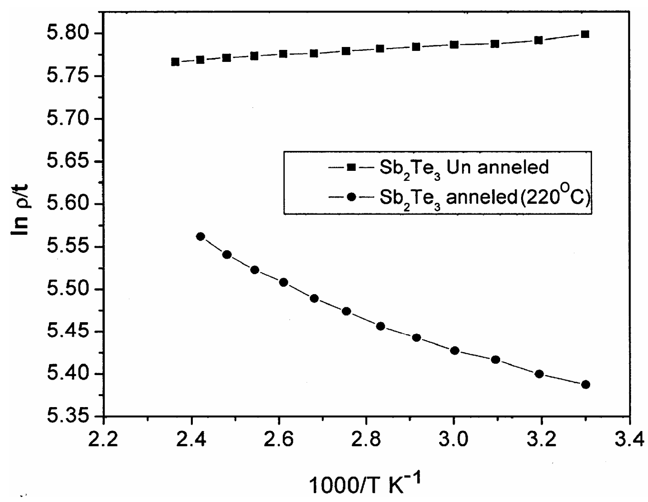

Fig. 6 — Sheet resistivity of unannealed and annealed Sb_2Te_3 thin film as a function of inverse of temperature

conducting behaviour with an activation energy of 0.046 eV.

2.4 Thermoelectric properties

The thermoelectric power (Seebeck coeff α) of each sample are calculated. For this measurement, the sample is arranged in such a way that one end is at the

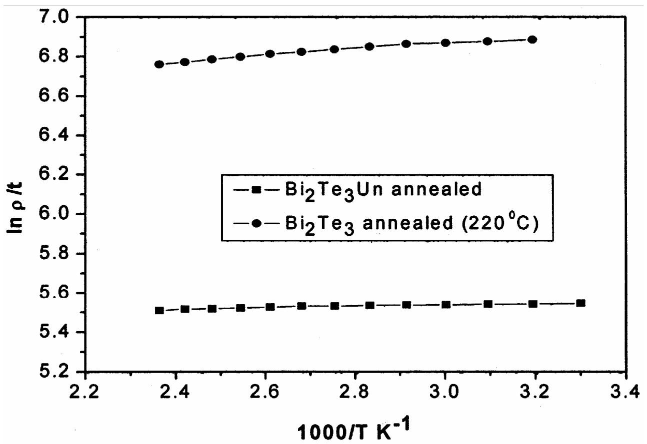

Fig. 7 — Sheet resistivity of unannealed and annealed Bi_2Te_3 thin film as a function of inverse of temperature

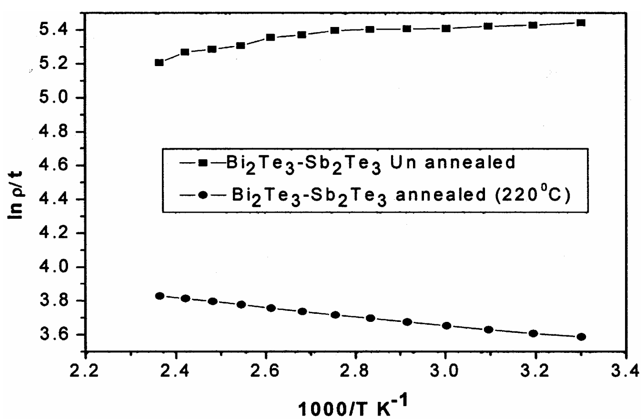

Fig. 8 — Sheet resistivity of Bi_2Te_3 – Sb_2Te_3 bilayer thin film as a function of inverse of temperature

hot junction and the other is at the cold junction. The temperature of the hot junction is varied successively. The thermoemf are noted for each value of hot junction temperature. From the thermo emf versus *dT* (difference between the temperature of two junctions) graph, the slope is determined which gives the thermo electric power (TEP) or the seebeck coefficient. For each sample, TEP versus T_h (hot junction temperature) is also plotted.

Figure 9 explains the variation of thermoelectric power of Sb_2Te_3, Bi_2Te_3 and Bi_2Te_3-Sb_2Te_3 bilayer thin films respectively at various temperature regions.

The figure of merit and the power factor are also calculated for each film. For antimony telluride a figure of merit of 0.17 is obtained. For the Bi_2Te_3 film and for the bilayer film, it is found as 0.43 and 0.49 respectively. The power factors are found as 0.8×10^{-3}, 1.74×10^{-3} and 2.24×10^{-3} $WK^{-2}m^{-1}$ respectively for Sb_2Te_3, Bi_2Te_3 and the bilayer films.

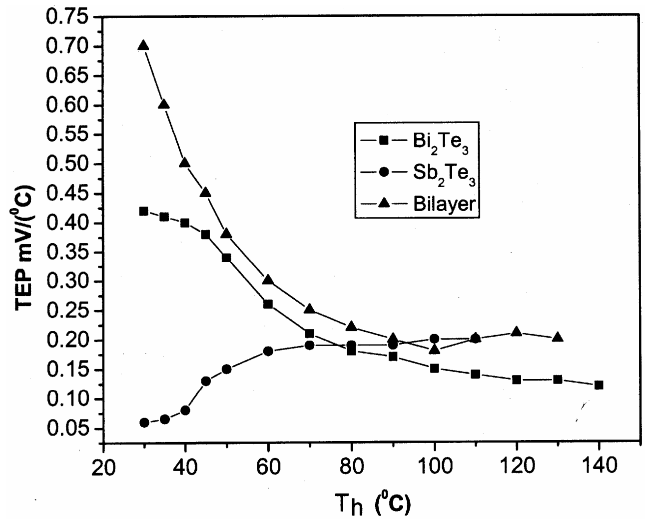

Fig. 9 — Thermo-electric power of Sb_2Te_3, Bi_2Te_3 and Bi_2Te_3-Sb_2Te_3

3 Results and Discussion

Sb_2Te_3, Bi_2Te_3 and Bi_2Te_3-Sb_2Te_3 thin films of various thickness are fabricated using thermal evaporation at vacuum. The X-ray diffraction patterns reveal their crystalline structure. From the conductivity studies it can be seen that the annealed Sb_2Te_3, and annealed bilayer film are showing conducting behaviour while the others are showing semiconducting behaviour. It is also observed that for the two single layer films, the activation energy is found to be increasing when annealed. But in the case of bilayer it is found that the activation energy is decreasing when annealed. This may be due to the diffusion of carriers between the layers. From the thermoelectric property studies, it has been found that the three kinds of thin film materials are of having the figure of merit $Z \leq 1$, as expected. Among these three, the bilayer of Bi_2Te_3 and Sb_2Te_3 is having larger value of figure of merit (0.49) which implies that it has higher thermoelectric performance than the others. This may be due to the change in the fermi surface by the diffusion of carriers between the thin film layers.

4 Conclusions

Thin films of tellurium alloys such as Sb_2Te_3, Bi_2Te_3 and their bilayer films are well established thermoelectric materials and are widely employed in thermoelectric generators and coolers. The Sb_2Te_3 film shows high thermoelectric behaviour at high temperature region while the Bi_2Te_3 film and the bilayer film show high thermoelectric behaviour at room temperature region as well as relatively low temperature regions. The thermoelectric performance will increase if we use the Bi2Te3-Sb2Te3 bilayer film instead of their single layer film.

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