Pramāṇa - J. Phys., Vol. 34, No. 3, March 1990, pp. 243-248. © Printed in India.

Electrical conductivity, thermoelectric power and figure of merit of doped Bi–Sb tapes produced by melt spinning technique

T K DEY

Cryogenic Engineering Centre, Indian Institute of Technology, Kharagpur 721 302, India

MS received 3 August 1989; revised 2 November 1989

Abstract. Temperature dependence of electrical conductivity and thermoelectric power are presented for In and Pb doped Bi + 8·28 at % Sb quenched tapes between 77 and 300K. The results are explained in terms of model for disordered semiconductors. Analysis of our data on electrical conductivity indicates the presence of a temperature independent part and a strongly temperature dependent part. While the T independent part originates from band conduction, the T dependent component could be understood considering the presence of localized states. Thermoelectric figure-of-merit of these tapes are also measured at 300K, which shows a large enhancement ($\sim 40\%$) over that reported earlier on thin Bi–Sb films. This suggests that doped Bi–Sb quenched tapes may be considered as a candidate for material in producing economic and light weight thermoelectric devices.

Keywords. Bismuth-antimony alloy; melt spinning technique; thermoelectric power; figure-of-merit; nearest neighbour hopping; localized states.

PACS Nos 70·20; 72·20

1. Introduction

Existence of a positive energy gap, high carrier mobility and low lattice thermal conductivity are some of the prime requirements for a useful thermoelectric material. This is because the figure-of-merit (Z) of thermoelectric material is expressed as

$$Z = S^2\sigma/K$$

where, S is the Seebeck coefficient, σ is the electrical conductivity and K is the thermal conductivity of the material. Bi–Sb alloys with Sb concentration between 4 and 40 at% meet most of the above requirements and hence, are regarded as an important system for thermoelectric energy conversion (Horst and Williams 1980). Efforts were made with Bi–Sb alloys for making thin film thermoelectric devices in the area of cooling (Trefny 1981), and radiation detector (Chopra and Pandya 1978) etc. Ion beam mixing of Bi–Sb alloys have been reported as a potential method for preparing thin film thermoelectrics (Benenson *et al* 1983; Ibrahim and Thompson 1985).

Melt spinning technique offers an inexpensive way for producing 20 to 30 μm thick Bi–Sb tapes. Most of the studies on this alloy have so far been concentrated either on crystalline bulk alloys (Smith and Wolfe 1962) or on thin films (Garcia *et al* 1972). Therefore, it is of interest to look for the extent to which the splat quenched Bi–Sb tapes prepared by melt spinning are suitable for thermoelectric applications, vis-a-vis thin films. In the present communication, we report our results on temperature dependence of electrical resistivity and thermoelectric power (TEP) of Bi–Sb tapes doped with small amount of In and Pb. In addition, room temperature data of figure-of-merit (Z) of these tapes are presented and compared with Z values of Bi–Sb films produced by different techniques.

2. Experimental

In and Pb doped Bi + 8·28 at% Sb tapes were prepared by melt spinning technique described elsewhere (Dey and Ghatak 1989). Electrical resistivity and TEP of these tapes were measured using four probe and differential methods respectively. Details of cryostatic arrangement and the experimental procedures were reported earlier (Dey *et al* 1985).

Figure of merit (Z) of the tapes were measured using modified Herman technique (Herman *et al* 1959; Trefny 1982). This involves the measurement of dc and ac resistivities of the tapes. Dc measurement simulates isothermal condition, while ac measurement with frequency higher than inverse of diffusivity simulates adiabatic condition. This requires frequency of only a few Hz in most cases. In the present study, ρ_{ac} was measured at 73 Hz. From these measurements, the figure of merit (Z) comes out as:

$$Z = (\rho_{ac}/\rho_{dc} - 1)T^{-1}$$

where, ρ_{dc} and ρ_{ac} are the dc and ac resistivities respectively and T is the temperature in K. Several corrections (Trefny 1982) are needed to obtain absolute values of Z. These correction factors are included in Z values reported for our tapes.

3. Results

Electrical resistivity (ρ) and TEP (S) of splat quenched Bi + 8·28 at% Sb tapes doped with small amount of In and Pb are shown in figures 1 and 2 respectively between 77K and 300K. All the tapes show an increase in resistivity with lowering of temperatures and finally approach a saturated value. This behaviour is similar to that reported earlier (Dey and Ghatak 1989) for undoped tapes of Bi–Sb alloys. However, doped tapes show higher resistivities compared to the undoped ones. Similar temperature dependences have been reported for vacuum deposited Bi–Sb films (Inoue *et al* 1979) and on Bi–Sb films deposited by ion beam mixing using Ag^+ and Kr^+ beams (Ibrahim and Thompson 1985). TEP of the tapes decrease with decrease of temperature and shows sign reversal (figure 2). The temperature at which the sign reversal occurs is dependent upon the composition of the tapes. N-type conductivity is apparent near room temperature for all the tapes. This behaviour of TEP is significantly different to that observed earlier for undoped Bi + 8·28 at% Sb tapes, where TEP was found to be negative over the entire temperature range. In addition, doping of Bi–Sb with In and Pb largely increases the magnitude of Seebeck coefficient at 300K. A maximum of $-118\,\mu$v/K has been observed for tapes containing 0·2 at%In, while for the tapes doped with 0·1 at% Pb a maximum of $-102\,\mu$v/K is obtained. These values may be compared with $-94\,\mu$v/K of undoped Bi + 8·28 at% Sb tapes (Dey and Ghatak 1989).

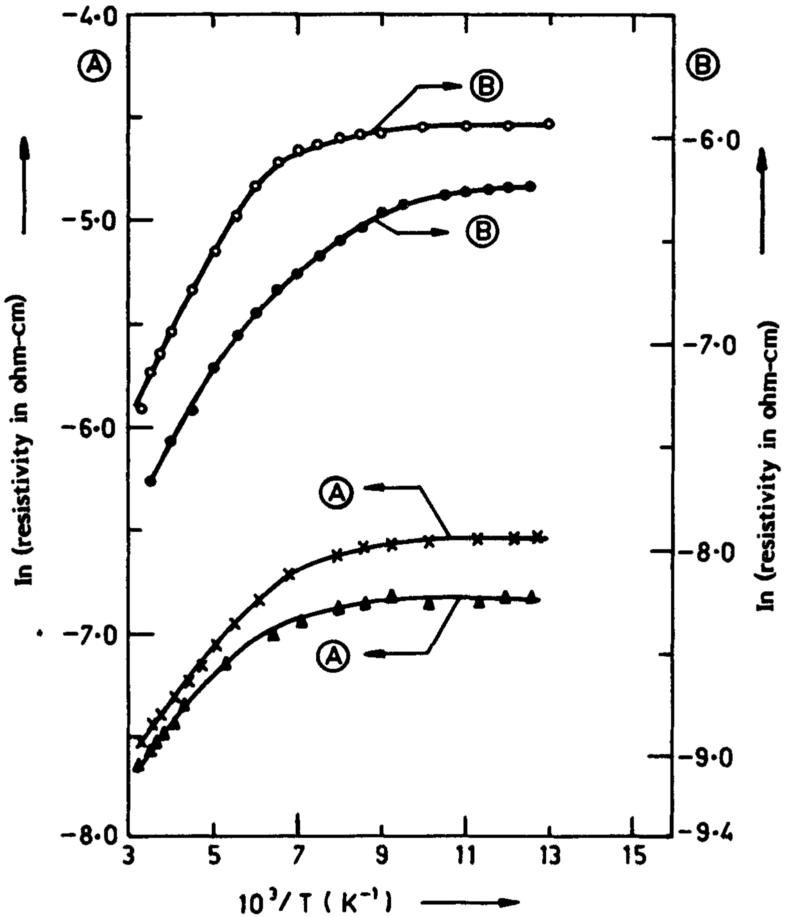

Figure 1. Ln (resistivity) as a function of reciprocal temperature for doped Bi + 8·28 at%Sb quenched tapes. (●) Bi–Sb (0·2 at%In), (○) Bi–Sb (0·3 at%In), (▲) Bi–Sb (0·1 at%Pb), and (×) Bi–Sb (0·2 at%Pb).

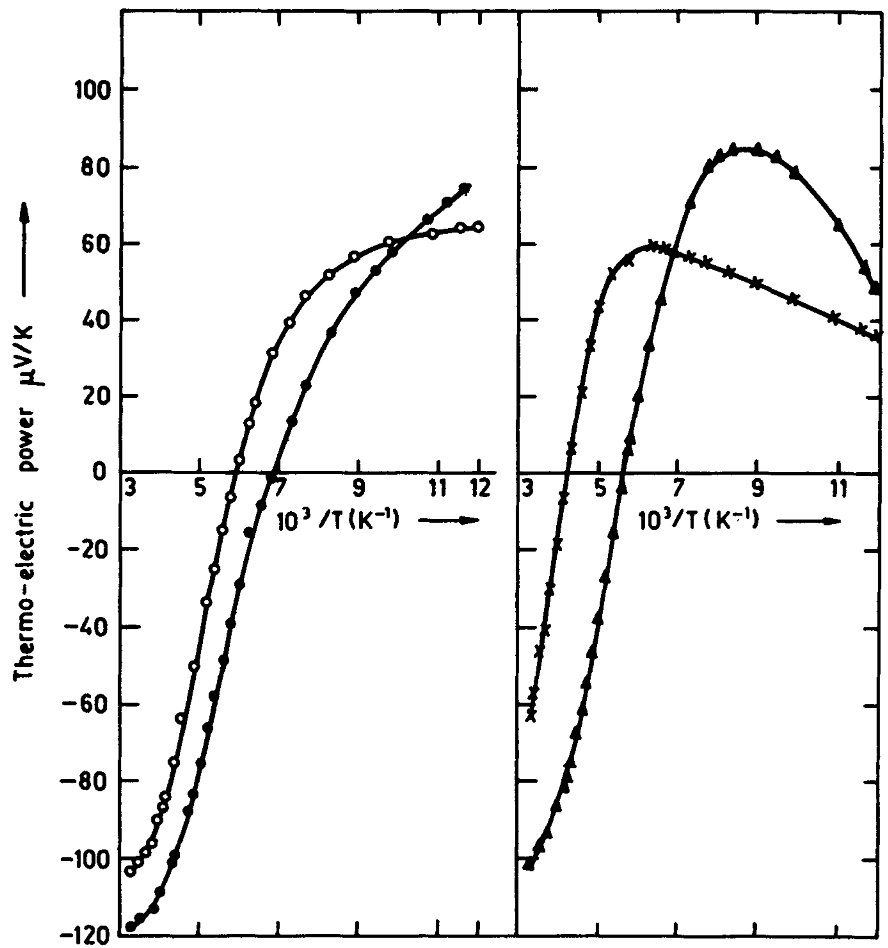

Figure 2. Thermoelectric power as a function of reciprocal temperature for doped Bi + 8·28%Sb quenched tapes. Legends same as in figure 1.

4. Discussion

Data on the temperature dependence of electrical conductivity has been analysed, assuming a temperature independent component (σ_0) and a strongly temperature dependent component (σ_h). The nature of origin of σ_0 and σ_h has already been discussed (Dey and Ghatak 1989), which relates to the formation of various types of structural imperfections due to rapid quenching. Such disorders are reported to lead to the formation of localized states in Bi–Sb tapes and in their thin films prepared by coevaporation (Inoue *et al* 1979). These localized states have very small mobility through which electrical conduction can occur. Depending upon the type of these states available or, formed, the temperature dependent component (σ_h) can have various temperature dependences (Mott and Davis 1971). For identifying the mechanisms responsible for electrical conduction in these tapes between 77K and 300K, we plotted ln σ_h against T^{-1} and $T^{-1/4}$. Only ln σ_h vs T^{-1} plots show linear behaviour with two different slopes (figure 3). In the temperature range from 300K and below the TEP sign reversal temperatures our data on doped quenched tapes can be described by the expressions (Mott and Davis 1970):

$$\sigma_h = \sigma_{ho} \exp[-(E_C - E_F)/kT]$$

$$S = -k/e[E_C - E_F/kT + A].$$

The activation energies (E_σ) calculated from the slopes ln σ_h vs T^{-1} plots at higher temperatures (figure 3) are nearly the same as calculated from the slopes of

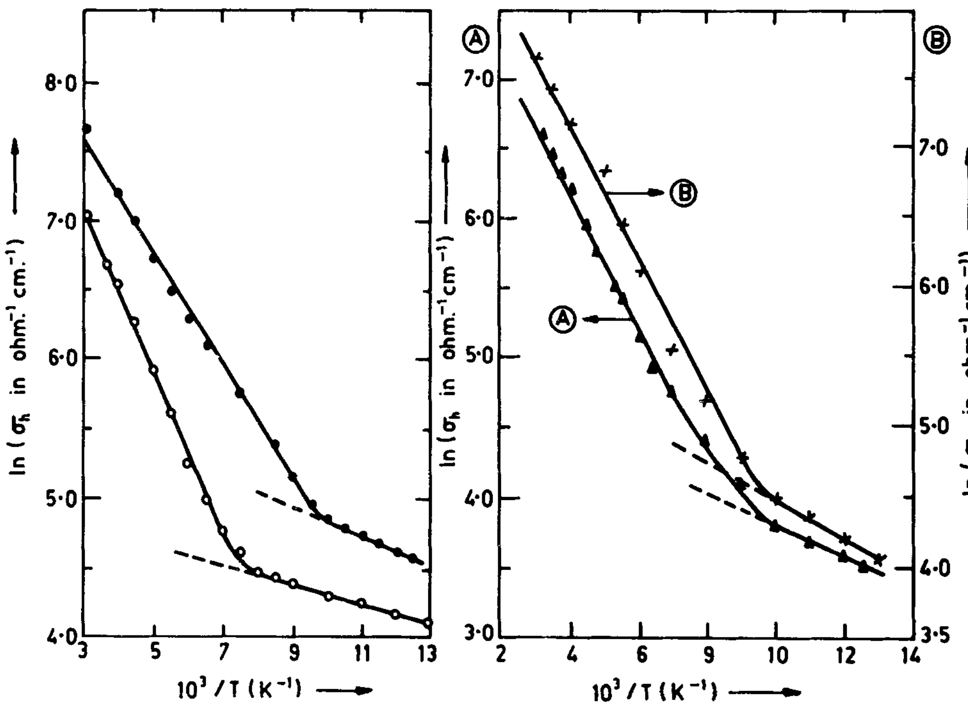

Figure 3. ln σ_h vs T^{-1} for (●) Bi–Sb (0·1 at % In), (○) Bi–Sb (0·3 at % In), (▲) Bi–Sb (0·1 at % Pb), (×) Bi–Sb (0·2 at % Pb), splat quenched tapes.

TEP vs T^{-1} plots (figure 2). These above features indicate that in this temperature range conduction takes place in only one band and the process is dominated by the carriers excited in the extended states beyond the mobility edge. Further lowering of temperature causes distinct change in slope of $\ln \sigma_n$ (figure 3), which shows that at low temperatures mechanism for electrical conduction is a different one. In addition, it may be noted that the slopes of $\ln \sigma_h$ vs T^{-1} lines are significantly smaller than that at higher temperatures. This clearly indicates that the conduction processes are associated with smaller activation energy. In a disordered system, such a situation can arise when conduction takes place due to either nearest neighbour hopping, or, by variable range hopping of carriers. In the present tapes variable range hopping is absent, since the data in this temperature range do not follow $T^{-1/4}$ dependence. For nearest neighbour hopping of carriers, electrical conductivity is given by the relation

$$\sigma_h = \sigma_{h'0} \exp[-\Delta W/kT]$$

where ΔW is the hopping activation energy. Further, TEP for nearest neighbour hopping should be proportional to temperature. Therefore, the linear region with reduced slope (figure 3) and the linearity of TEP with temperature observed in our tapes are indicative of nearest neighbour hopping of carriers (holes). The hopping activation energy calculated from figure 3 are given in table 1.

Table 1.

Samples (Bi + 8·28 at % Sb + x)	TEP (300 K) μV/K	E_σ (eV)	E_s (eV)	ΔW (eV)	Carrier type
$X = 0{\cdot}2$ at % In	−118	0·0400	−0·0417	0·0098	n, $T > 145$ K p, $T < 145$ K
$X = 0{\cdot}3$ at % In	−104	0·0546	−0·0444	0·0054	n, $T > 166$ K p, $T < 166$ K
$X = 0{\cdot}1$ at % Pb	−62	0·0452	−0·0450	0·0100	n, $T > 154$ K p, $T < 154$ K
$X = 0{\cdot}2$ at % Pb	−101	0·0460	−0·0400	0·0132	n, $T > 285$ K p, $T < 285$ K

Table 2.

Samples	Method of preparation	Figure of merit (Z) $\times 10^{-4}$ (deg^{-1})
Bi thin film	Ion beam mixing	2·26
$Bi_{87}Sb_{13}$ thin film (Sn doped)	Ion beam mixing	3·33
Bi tapes	Melt spinning	2·46
Bi + 8·28 at % Sb	Melt spinning	3·04
Bi + 8·28 at % Sb (0·2 at % In)	Melt spinning	4·58
Bi + 8·28 at % Sb (0·3 at % In)	Melt spinning	4·80
Bi + 8·28 at % Sb (0·1 at % Pb)	Melt spinning	3·79
Bi + 8·28 at % Sb (0·2 at % Pb)	Melt spinning	4·24

The results of figure of merit (Z) of our quenched Bi–Sb tapes measured at 300K are given in table 2 along with the Z values for Bi–Sb thin films (Ibrahim and Thompson 1985). Figure of merits (Z) of doped Bi + 8·28 at% Sb tapes are found to exceed that for undoped ones. Further, it is interesting to note that for In doped Bi–Sb tapes an increase of Z value by $\sim$40% over that of Sn doped Bi–Sb films has been observed. Such a large increase in Z observed for doped Bi–Sb quenched tapes results primarily from their higher TEP. However, other feature contributing towards increased Z probably comes from finer grains in liquid quenched tapes, which helps to reduce its thermal conductivity (K) through enhanced phonon-grain boundary scattering (Rowe and Bhandari 1985).

5. Conclusion

Temperature dependence of electrical resistivity and TEP of In and Pb doped Bi–Sb quenched tapes between 77K and 300K have been explained considering the formation of localized states near the band edges. These states are formed as a consequence of various structural disorders associated with rapid quenching. A dominant n-type conduction by carriers excited to the extended state at higher temperatures which makes a transition to P-type hopping near the Fermi level at lower temperatures are concluded from our data. Substantial enhancement of figure of merit has been observed in doped quenched Bi–Sb tapes compared to that for doped Bi–Sb thin films. This suggests that economical device development using Bi–Sb may well be based on quenched tapes processing rather than thin film technology.

Acknowledgements

The author wishes to acknowledge the technical help rendered by Mr D K Paul of Cryogenic Engineering Centre. This work was funded by CSIR (New Delhi).

References

Benenson R E, Tikku V K, Kollewe D and Jin H S 1983 *Nucl. Instrum. Methods* **209/210** 185
Chopra K L and Pandya D K 1978 *Thin Solid Films* **50** 81
Dey T K, Chatterjee C and Duttagupta B 1985 *Proc. Int. Conf. Cryogenics* p. 435
Dey T K and Ghatak S K 1989 *Pramāṇa – J. Phys.* **32** 161
Garcia N, Kao Y H and Strongin M 1972 *Phys. Rev.* **B5** 2029
Herman T C, Chan J H and Logan M J 1959 *J. Appl. Phys.* **30** 1351
Horst R B and Williams L R 1980 *Proc. 3rd Int. Conf. Thermoelectric Energy Conversion* p. 139
Ibrahim A M and Thompson D A 1985 *Nucl. Instrum. Methods* **B7/8** 566
Inoue M, Urai N and Yagi H 1979 *Surf. Sci.* **86** 369
Mott N F and Davis E A 1971 *Electronic Processes in Non crystalline Solids* (Oxford: Clarendon Press) p. 201
Rowe D M and Bhandari C M 1985 *Appl. Phys. Letts.* **47** 255
Smith G E and Wolfe R 1962 *J. Appl. Phys.* **33** 841
Trefny J U 1981 *Proc. 16th Intersoc. Energy Conversion Engg. Conf.* p. 2019
Trefny J U 1982 *Proc. 4th Int. Conf. Thermoelectric Energy Conversion* p. 79