CHAPTER-8

TRANSPORT PROPERTIES OF $Bi_{1-X}Sb_X$ SINGLE CRYSTALS

This chapter reports the results obtained on the transport properties of $Bi_{1-x}Sb_x$ (x = 0.05,0.10, 0.15,0.20,0.25,0.30) single crystals. The chapter is divided into three parts. Part-A deals with Hall measurements, Part B deals with the Seebeck effect and Part C deals with temperature dependence of electrical resistivity.

The Electrical properties are one of the characteristics that determine the metallic, semi conducting or insulating nature of the material. A semiconductor is often defined as having an electric conductivity between that of an insulator and a metal. The properties generally termed as electrical properties include electrical resistivity, Hall coefficient, the carrier density and type, Hall mobility of the carriers, magneto-resistivity and the thermoelectric power.

Part A: Hall measurement:

The Hall measurements were carried out at room temperature, using Van der Pauw method[1], employing linear four probe geometry, Charge carriers contributing to current caused by an applied electric field are deflected by a magnetic field applied perpendicular to the current. The resulting Hall voltage normal both to the current and the field can be measured. The sample is kept between the two poles of a strong electromagnet capable of producing magnetic field of the order of 18 kilo gauss. A sensitive current meter is connected in series

with a stabilized D.C. power supply and the sample. Across the other two contacts, digital micro voltmeter is connected. Current and voltage are measured in absence and presence of the applied magnetic field.

A large number of samples were measured at room temperature . The Hall co-efficient, mobility and carrier concentration of $Bi_{1-x}Sb_x$(x= 0.05,0.10,0.15,0.20,0.25,0.30) are listed in Table-1. The mobility calculations have been based on the resistivity data (part c). The Hall coefficient was found to be negative indicating that the majority charge carriers are electrons and thus the material is n-type semiconductor for x value as mentioned above.

Table- 1

Materials	Hall Co-efficient , R_H (cm^3/colomb)	n (carrier concentration) cm^{-3}	Carrier Mobility Cm^2/v.sec.
$Bi_{0.95}Sb_{0.05}$	2.82×10^{-4}	2.23×10^{22}	3246
$Bi_{0.90}Sb_{0.10}$	2.38×10^{-3}	2.71×10^{21}	2635
$Bi_{0.85}Sb_{0.15}$	2.00×10^{-3}	2.21×10^{21}	2240
$Bi_{0.80}Sb_{0.20}$	2.42×10^{-4}	2.72×10^{21}	2754
$Bi_{0.75}Sb_{0.25}$	2.81×10^{-4}	2.23×10^{22}	3203
$Bi_{0.70}Sb_{0.30}$	1.68×10^{-4}	3.72×10^{22}	4152

To check whether the material is p type or n-type, we also used hot probe method. In this method a sample is connected with ballistic galvanometer

through one hot contact and the other cold contact. The hot probe would diffuse the majority carriers in the specimen to the cold contact and accordingly the current direction in the circuit is set-up. The galvanometer deflection indicated the carriers to be electrons. Thus the samples were found to be n-type.

Thermo electric measurement:

In recent years a significant part of the nation's total research and development effort have been devoted to various methods of energy conversion. Presently, the most advanced schemes are thermoelectricity, thermionics, fuel cells and magneto hydrodynamics. Each of these forms will almost certainly have its place in future energy production. Thermoelectricity has now reached a state where a reasonably systematic presentation can be made of its various aspects.

Interest in the Bi –Sb material system has recently been stimulated by the promise of new generation of thermoelectric materials based on these alloys [2-7]. Bismuth and antimony are both semi-metal, while $Bi_{1-x}Sb_x$ alloy is a semiconductor in the composition range $0.05 < x < 0.22$[5].

With properties such as small band gap, high mobility and a reduced lattice thermal conductivity, semi conducting $Bi_{1-x}Sb_x$ alloy may potentially be used as an n-type thermo element operating around 80 K. The thermoelectric figure of merit for $Bi_{1-x}Sb_x$ ($0.09<x<o.15$) has been reported to be 0.88 at 80 K in a magnetic field of 0.13 T [8].. There have been several measurements by earlier workers on $Bi_{1-x}Sb_x$ [9-17]. Theoretical calculations have predicted that bismuth and its related alloys are promising for low dimension TE materials at 100 K[18-19].

The experimental set up used for determination of thermoelectric power (TEP) is shown in figure 1. One can measure TEP directly from Thomson coefficient (σ) but it is not easy to measure σ. The principle being followed for measurement of TEP is to create a desired temperature gradient between the copper block using the heated coil made up of manganin wire, which is controlled by a temperature controller. The sample is placed in between the copper blocks. The sample was a carefully cleaved crystal plate along (111).The sample can have any size but it was of thickness of about 1-3 mm so that the distance between the copper blocks and temperature gradient can be optimally maintained. The temperature gradient was measured using calibrated thermocouple pairs made up of Au-Fe (7%) – Chromel. To avoid the direct electric contact between the thermocouple and Cu block, thermocouple comes coated with an electrically insulating but thermally conductor material. The voltage developed across the two Cu blocks is measured. For measuring the temperature gradient the voltage developed across thermocouple has to be measured. By using a scanner the two voltages are measured sequentially by a single voltmeter having accuracy of a nanovolt. For achieving low temperature, a CCR (Closed cycle Refrigerator) is used.

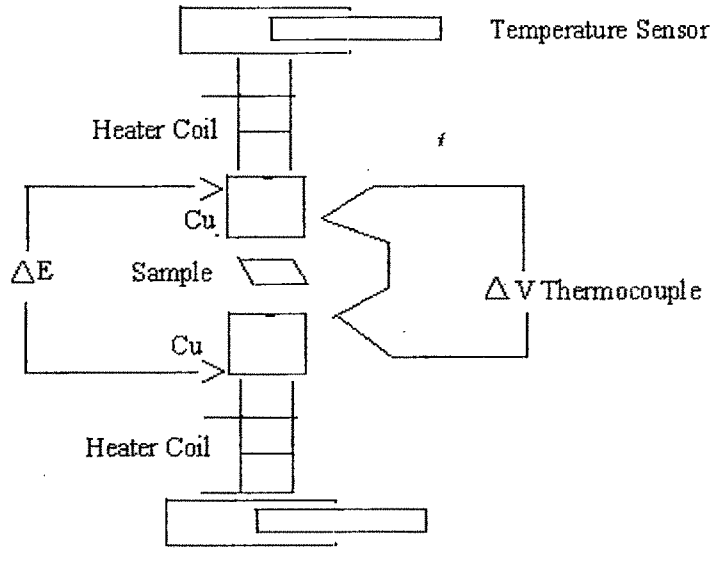

Figure - 1 Block diagram of sample holder of TEP set up

Experimental Discussion:

If a temperature gradient is maintained between two ends of a conductor, a thermo emf will be developed across it and this effect is called Seebeck effect or thermoelectric effect. If ΔT is the temperature gradient across the sample and ΔV is resultant voltage developed because of this temperature gradient, then thermoelectric power is defined as

$$S = \delta V / \delta T$$

so that the energy difference between cold and hot ends is given as

$$\Delta U = (\delta U / \delta X)\, \Delta X$$

As the electrons flow from hot end to cold end to minimize their energy, there will be an electric field generated across the conductor.

The phonon contribution to heat capacity at low temperature may be approximated as $C_v = \beta T^3$ and one finds a T^3 variation in S. Using the Seebeck effect, thermal energy (heat) can be converted into electric energy, which is called thermoelectric power generation. When temperature gradient is maintained across two ends of the sample, the thermoelectric voltage is produced in proportion to the temperature gradient.

If a load is connected to the sample, the electric power is consumed by the load. Here the thermoelectric power corresponds to the electromotive force and the resistivity corresponds to the internal resistance. Advantages of thermoelectric power generation are maintenance free electric power source, energy recovery from waste heat and long operating lifetime.

In figures 2, 3, 4, 5 and 6 the TEP values for the $Bi_{1-x}Sb_x$ (X= 0.05.0.10,0.15,0.25,0.30) single crystals are plotted as functions of temperature between 300 K to 400 K. The TEP of pure Bi crystal was found to be in good agreement with the previous report [20-21]. The addition of Sb into Bi affects the TEP value. As the Sb concentration increases, the magnitude of the TEP increases. The maximum magnitude of TEP was obtained between 340 K and 360 K for x= 0.15,0.25 and 0.30 and around 330 K for x= 0.05 and 0.10.

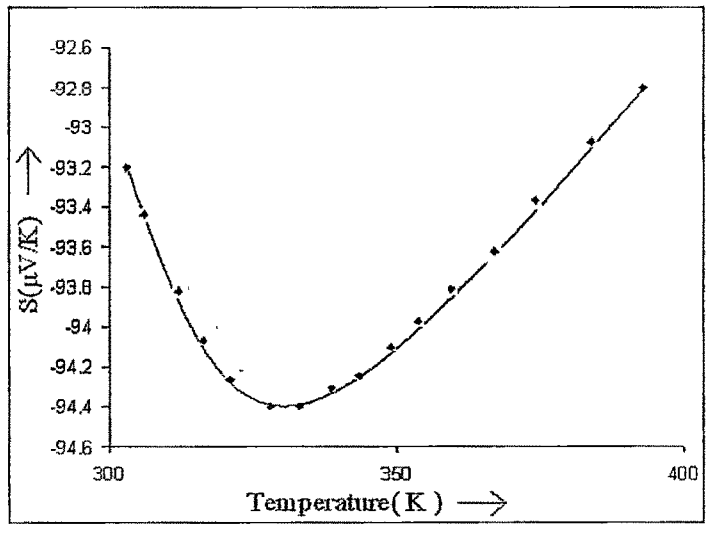

Figure-2 $Bi_{0.95}Sb_{0.05}$

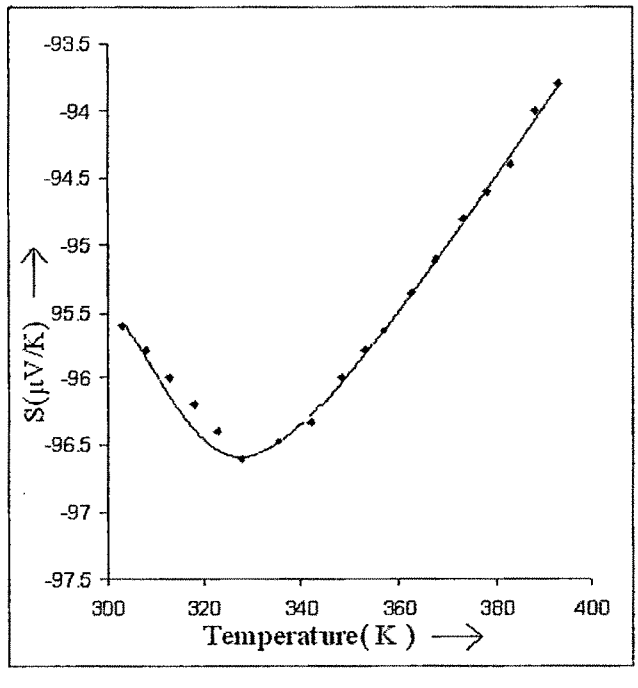

Figure-3 $Bi_{0.90}Sb_{0.10}$

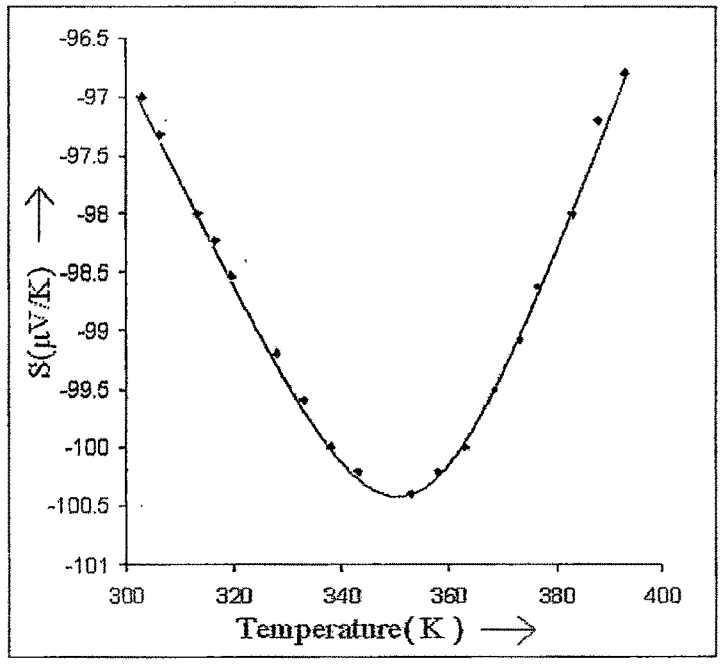

Figure-4 $Bi_{0.85}Sb_{0.15}$

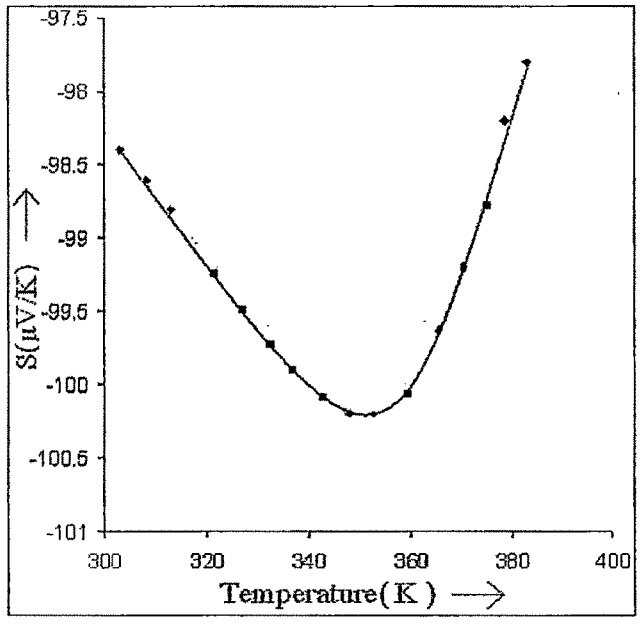

Figure-5 $Bi_{0.75}Sb_{0.25}$

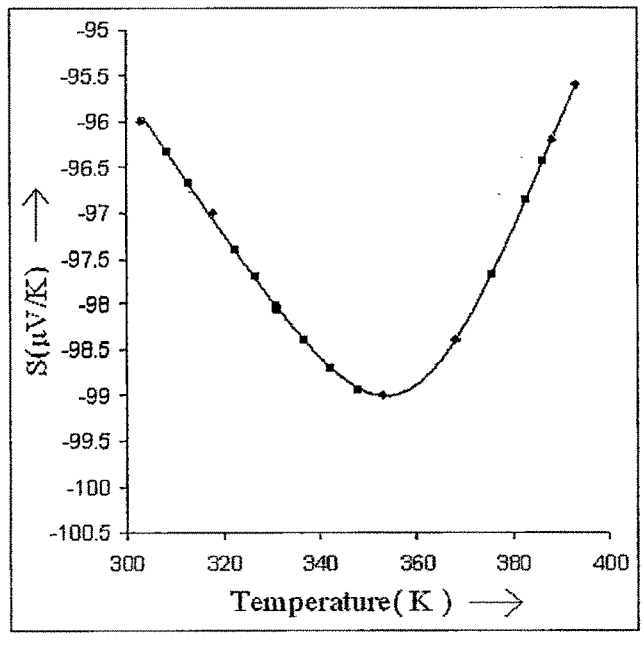

Figure-6 $Bi_{0.70}Sb_{0.30}$

For a thermoelectric material containing both electron and holes, the total TEP may be modeled by the relation,

$$S= (\sigma_e S_e +\sigma_p S_p)/ (\sigma_e +\sigma_p)$$

where σ_e and σ_p are the electrical conductivities and S_e and S_p are the TEP's for electrons and holes, respectively. The observed negative TEP implies a higher mobility for electrons than holes [22]. The magnitude of the TEP increases with decreasing temperature above certain temperature. This increase is due to the freeze-out of electrons and holes.

Resistivity of the crystal:

Valde's four probe method has been used for the measurement of electric conductivity of the crystals. The advantage of this technique is that one can use samples of any arbitrary shape. The problems of contact resistance, heating effect and contamination are avoided by using the four collinear pressure contacts on the surface. A cleaved sample with thickness 0.7 mm was kept on the base plate of the sample holder. The four probes were allowed to rest under spring pressure on the middle of the sample. The current was adjusted to a desired constant value, I, through the two outer probes and the corresponding voltage, V, across the inner pair was measured. The whole set up was kept in an oven. The rate of heating was kept at about 5°C/min. The temperature was sensed by a thermometer of least count 1°C. The distance between the successive probes was 1.8 mm approximately. The formula to determine the resistivity is,

$$\rho_o = (V/I) \times 2\pi S$$

where, S is mean probe separation, ρ_o is resistivity . Since the thickness of the sample was not larger than the probe separation, a correction factor has to be applied giving resistivity to be

$$\rho = \rho_o \ / J_7 (W/S)$$

where, W is thickness of the sample and the correction factor J_7 (W/S) was obtained from the table for the appropriate value of (W/S)[23].

The measurements were carried out at different temperatures in the range of 200 to 400 K. The room temperature resistivity values of $Bi_{1-x}Sb_x$ (x= 0.05,0.10,0.15,0.20,0.25,0.30) are in Table 2.

The resistivity as a function of temperature is shown in the plot of ln ρ Vs 1/T, shown in figures 7-12.The activation energy obtained from these plots and given by the relation

$$\rho = \rho_o e^{(-Ea/KT)}$$

where, ρ = Resistivity at particular temperature, ρ_o = Resistivity at room temperature and E_g = Activation energy, is tabulated in Table -3. The value has no significant effect of Sb concentration as expected of a degenerate semiconductor.

It is also observed that the resistivity decreases with increasing temperature implying semiconducting nature. However at the same time, increase of Sb content causes increase in resistivity.

Table-2

Materials	Resistivity μΩ · cm
$Bi_{0.95}Sb_{0.05}$	116
$Bi_{0.90}Sb_{0.10}$	186
$Bi_{0.85}Sb_{0.15}$	230
$Bi_{0.80}Sb_{0.20}$	302
$Bi_{0.75}Sb_{0.25}$	336
$Bi_{0.70}Sb_{0.30}$	371

Table 3

Materials	Activation energy (Eg)
$Bi_{0.95}Sb_{0.05}$	0.024 eV
$Bi_{0.90}Sb_{0.10}$	0.028 eV
$Bi_{0.85}Sb_{0.15}$	0.029 eV
$Bi_{0.80}Sb_{0.20}$	0.027 eV
$Bi_{0.75}Sb_{0.25}$	0.026 eV
$Bi_{0.70}Sb_{0.30}$	0.025 eV

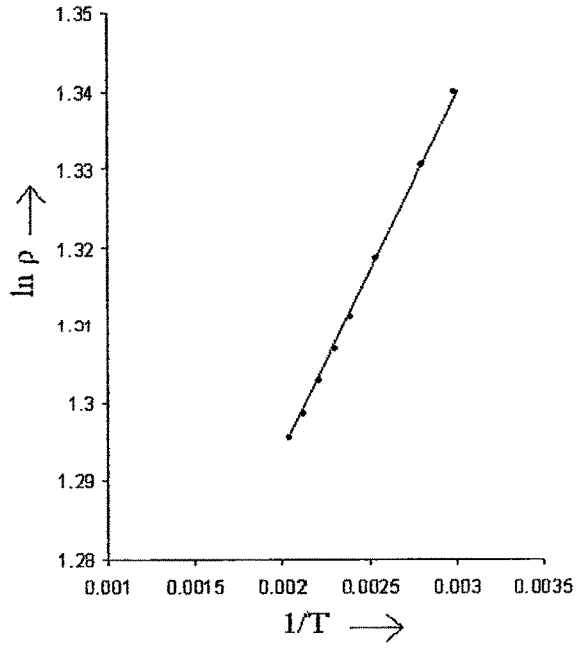

Figure-7 $Bi_{0.95}Sb_{0.05}$

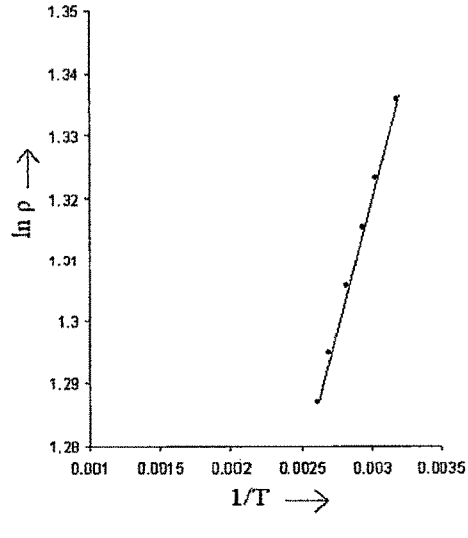

Figure-8 $Bi_{0.90}Sb_{0.10}$

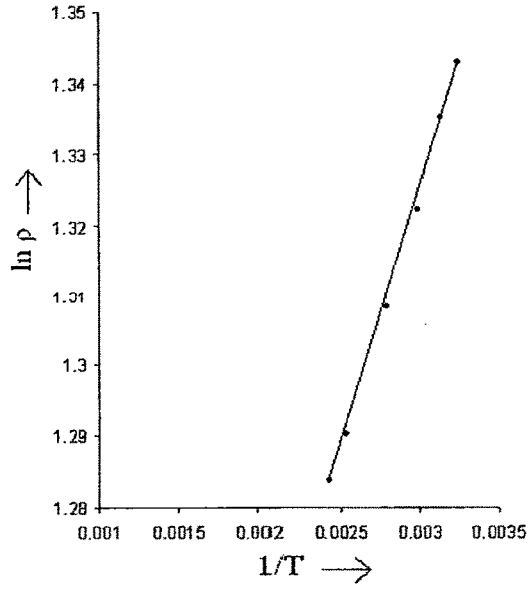

Figure-9 $Bi_{0.85}Sb_{0.15}$

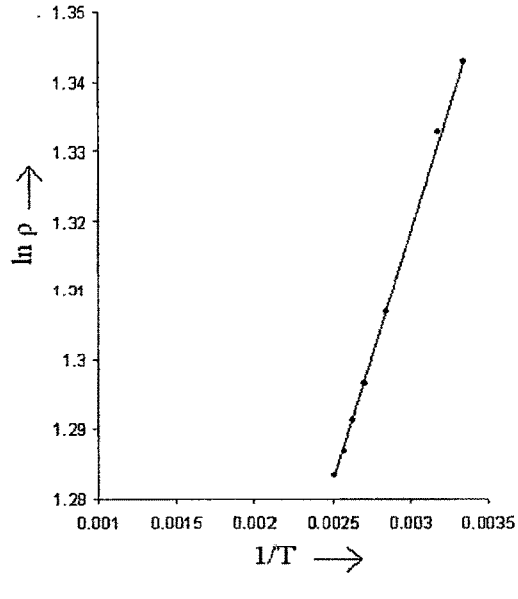

Figure-10 $Bi_{0.80}Sb_{0.20}$

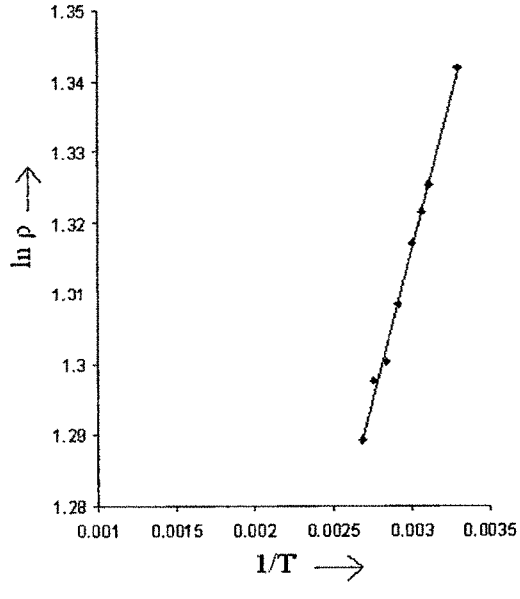

Figure-11 $Bi_{0.75}Sb_{0.25}$

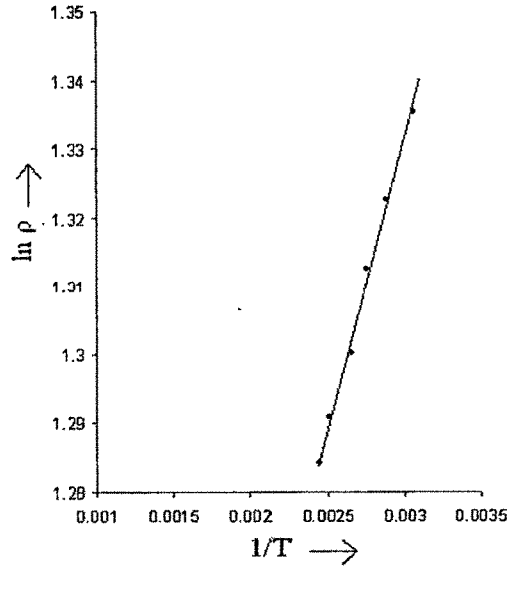

Figure-12 $Bi_{0.70}Sb_{0.30}$

Conclusions:

1 The sign of Hall coefficient and thermal EMF and the results of the hot probe tests show that all the crystals are of n-type, with carrier concentration of the order of 10^{21} cm^{-3} to 10^{22} cm^{-3}.

2 The room temperature resistivity of $Bi_{1-x}Sb_x$ single crystals was found to increase from above 116 μΩ·cm, to 371 μΩ·cm with x increasing from 0.05 to 0.30.

3 The resistivity activation energy of $Bi_{1-x}Sb_x$ single crystals is on average 0.026 eV.

4 With increase in Sb concentration the resistivity of crystals increases.

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