CHAPTER – 8

TRANSPORT AND OPTICAL PROPERTIES OF CRYSTALS

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The tellurides of bismuth and antimony are narrow band gap degenerate semiconductors and are very important thermoelectric materials; hence their transport properties are the most important ones to be studied. As discussed earlier Bi_2Te_3 is known to have better parameters with regard to thermoelectric applications as compared to those of Sb_2Te_3.

Some important results found in literature are outlined below. Bi_2Te_3 is a p-type semiconductor. At room temperature the thermoelectric power perpendicular to the c-axis is 218 μV/°K [2]. Its electrical resistivity is about 1.6×10^{-5} ohm-m [1]. At room temperature, the Hall coefficient and carrier concentration are 0.42×10^{-5} m^3/A sec and 1.7×10^{25} m^{-3}, respectively [1-2]. P. Lostak et al have reported experimental data on optical properties (transmission and reflection spectra) and transport coefficients of $Sb_{2-x}In_xTe_3$ single crystals and their mutual comparison with the aim to evaluate their relation to point defects in these crystals [3]. Heon Phil Ha et al [4] have reported the effect of excess tellurium on the thermoelectric properties of Bi_2Te_3-Sb_2Te_3 solid solutions.

They found that growth speed and excess amount of Te are important in optimizing the figure of merit. When the process parameters were optimized, a maximum figure of merit 2.95 X 10^{-3} K^{-1} was obtained for the crystals grown by the zone melting method at a rate of 0.1 mm/ min and with the composition 22.5 wt% Bi_2Te_3 and 77.5 wt% Sb_2Te_3 with 5 wt% excess Te in the melt [4].

J.Sramkova et al [2] have reported room temperature value of Hall constant R_H (B || C) , Seeback coefficient α , and temperature dependence of electrical conductivity $\sigma_{\perp c}$ in the 120 -360 K temperature interval,in the case of $Bi_{2-x}In_xTe_3$ crystals. The variation of the Hall constant and Seeback coefficient with increasing indium content in the $Bi_{2-x}In_xTe_3$ samples showed that on exceeding a certain limiting concentration of indium, the conductivity changes from p-type to n-type [5-6].

Agarwal et al have reported measurements of thermoelectric power and resistivity which enabled the determination of both carrier mobility and carrier concentration of tin monoselenide semiconductor [7]. Desai et al have reported Hall measurement on the cleavage faces of doped Bi_2Te_3 single crystals obtained by Bridgaman method [8].

Effect of addition of indium in Sb_2Te_3 has been studied by various workers. P.Lostak et al [3] is a good example which reports the optical properties (transmission and reflection spectra) and transport coefficients of $Sb_{2-x}In_xTe_3$ single crystals and their mutual comparison with an aim to evaluate their relation to point defects in these crystals.

The present author has carried out studies on electrical resistivity, Hall effect, thermoelectric power and optical band gap of the crystals under study, namely, $In_xBi_{2-x}Te_3$ with($x = 0.1, 0.2$ and 0.5). The results are discussed below.

ELECTRICAL PROPERTIES :

A. Resistivity of the crystal:

Valde's four probe method has been used for the measurement of electrical 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 four colinear pressure contacts on the surface. A schematic of the contact array is shown in Figure – 1.

A freshly cleaved sample with thickness approximately 0.5 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 average distance between the successive probes was 2 mm. The resistivity is then calculated as :

$$\rho_0 = \frac{V}{I} \times 2 \pi S \qquad \ldots\ldots 1$$

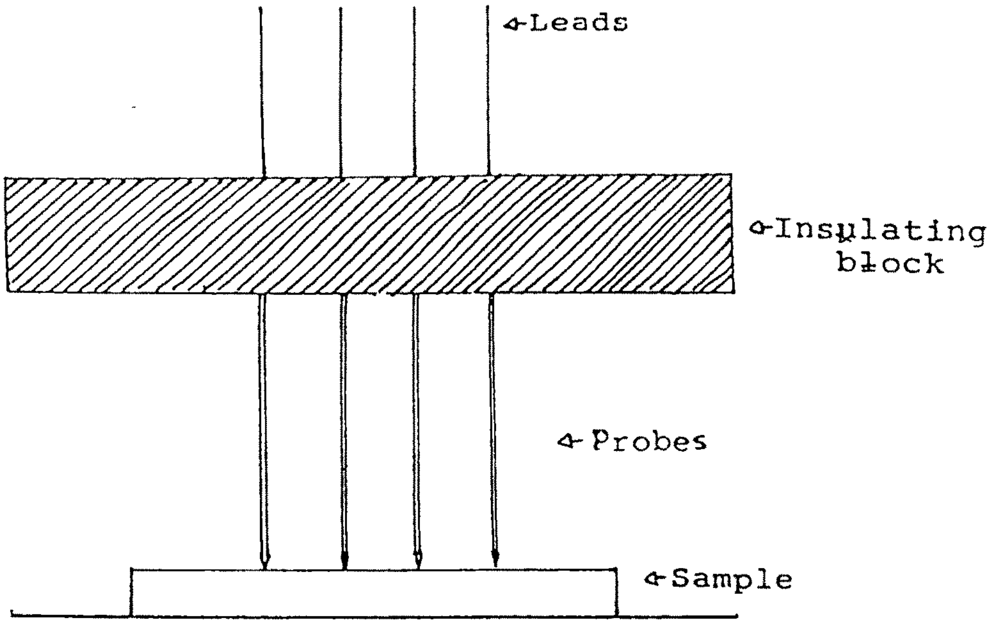

Figure - 1 : A schematic of the contact-array in Valde's set up.

where, S = mean probe separation, ρ_0 = resistivity. Since the sample thickness was not too larger than the probe separation, a correction factor has to be applied giving resistivity to be

$$\rho = \frac{\rho_0}{G_7(w / s)} \qquad \ldots\ldots2$$

where, w = thickness of the sample and the correction factor G_7 (w / s) was obtained from the table for the appropriate value of (w/s)[9].

The conductivity type of the crystal was tested by the hot probe method. $In_{0.1}Bi_{1.9}Te_3$ exhibited p-type while $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ exihibited n-type conductivity. The resistivity measurements were carried out along the cleavage faces of the crystals, at different temperatures in the range from 35°C to 130°C.

The room temperature resistivities of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ were measured to be 0.0244, 0.0246, 0.0249 ohm - cm, respectively. The temperature dependence of the resistivity ρ of the three crystals is shown in the respective plots of ln (resistivity) versus inverse temperature in Figure-2. Similar trends at and near room temperature have been reported for p-type Bi_2Te_3 thin films[10] and p-type $Bi_2Te_{2.8}Se_{0.2}$ single crystals[11], indicating extrinsic conduction to be dominating in the temperature range used. The plots obey the relation (3).

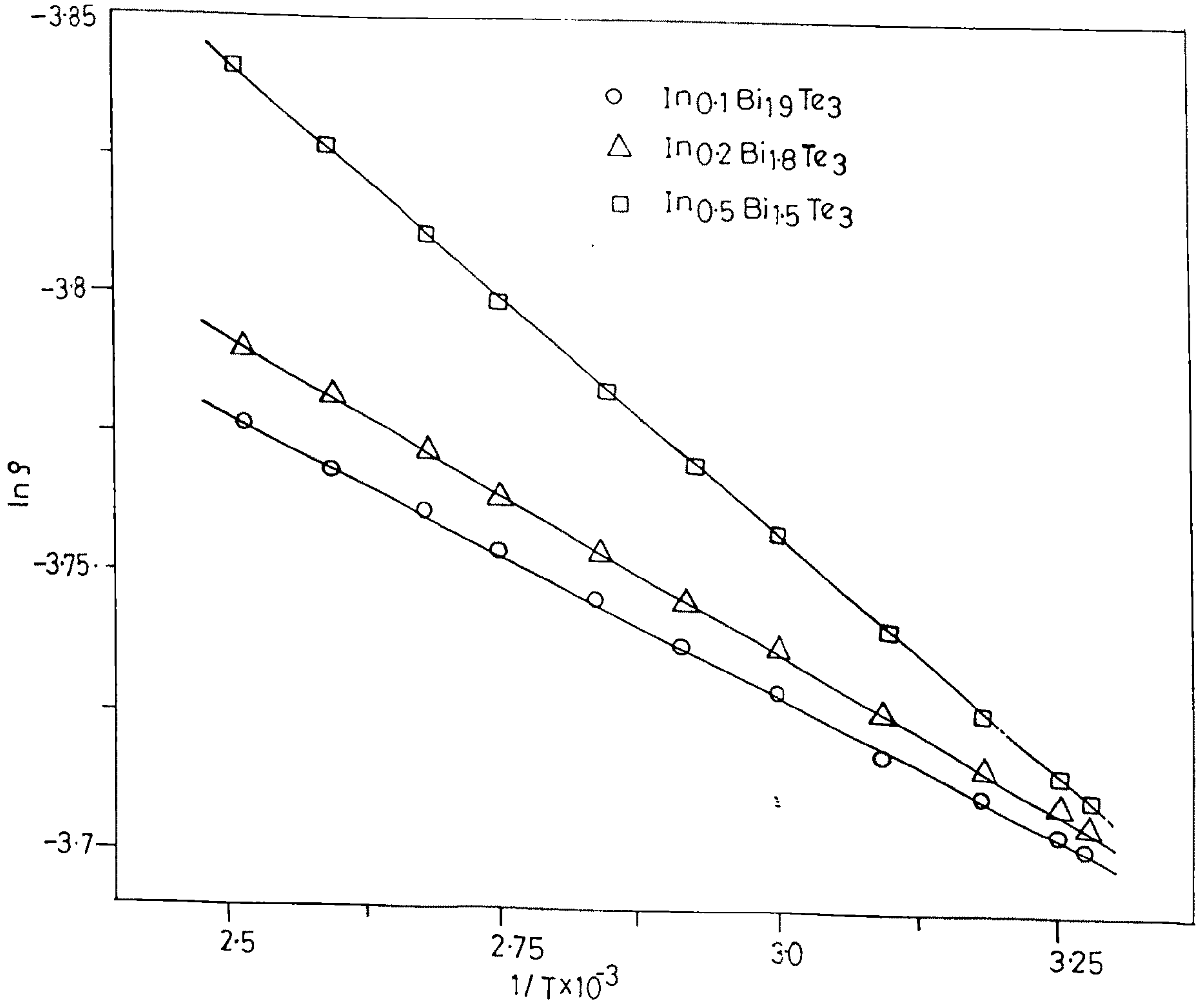

Fig.2.: Plots of ln ρ vs 1/T

$$\rho = \rho_0 \exp(-E\rho / K_B T) \qquad \text{---------3}$$

where E_ρ = Resistivity activation energy, K_B = Boltzmann constant and T = absolute temperature.The activation energy values calculated from the corresponding slopes are found to be .015,0.0198 and 0.028 eV respectively. The values show an increase with In content in the crystals. Such a resistivity variation with temperature is explained by the presence of traps for electrons in the forbidden gap or by the formation of additional acceptors at high temperature [7-9]. The intrinsic conduction may set in at temperatures higher than those used in the present investigation.

Hall Measurement :

The Hall measurements were carried out at room temperature, using Van der Pauw method. The probes 1 & 2 (as shown in Figure 3) were connected to a power supply with a digital current meter in series and across the probes 3& 4, a digital microvoltmeter was connected to measure the voltage. The crystal was placed between the poles of a strong electromagnet giving a field of about 18 K gauss maximum. The current and voltage were measured with and without the magnetic field. A large number of samples were measured at room temperature. The Hall coefficient, mobility and carrier concentration of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ crystals are listed in Table-1. The change- over of conductivity type from p-type to n-type with varying In concentration in this psuedobinary system has also been

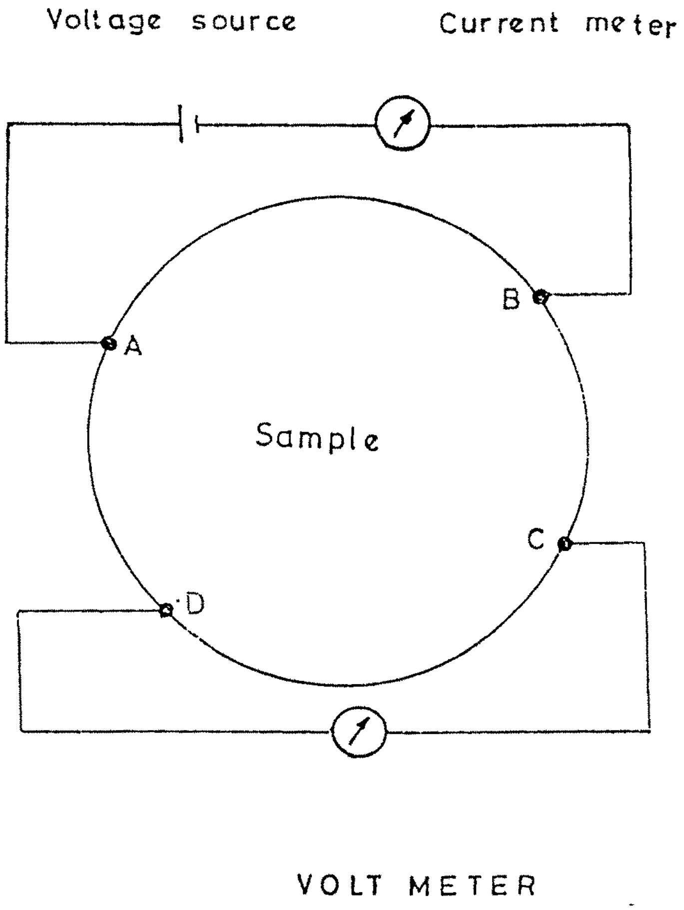

Figure .3. : Circuit diagram for resistivity measurement through Van der Pauw method.

Table – 1

Crystal	Hall Co-efficient cm^3/coul	Carrier Mobility cm^2/V-sec	Carrier Concentration 10^{19}cm^{-3}	Conductivity type
$In_{0.1}Bi_{1.9}Te_3$	0.1307	5.83	4.78	p
$In_{0.2}Bi_{1.8}Te_3$	0.1934	7.86	3.23	n
$In_{0.5}Bi_{1.5}Te_3$	0.8256	33.157	0.757	n

reported by L.Jansa and L.Koudelka [6]. This interesting phenomenon is reconfirmed in the present observation as seen above. A finer variation of In concentration has been carried out by L.Jansa et al [2]. They have concluded that when 'x' exceeds 0.1 in $In_xBi_{2-x}Te_3$ the conductivity changes from p-type to n-type.The results obtained in present study are consistent with their findings. The antisite defects in these crystals have been shown to play a crucial role in this respect. The substitutional defects of In on Bi sites (existing in these crystals) are supposed to carry a partial positive change which increases the bond polarity in the Bi_2Te_3 structure. This in turn decreases the concentration of the antisite defects of Bi on Te sites. Hence the acceptor levels decrease in concentration. The transition from p-type to n-type itself is however connected with negatively charged Bi vacancies and positively charged Te vacancies as suggested by Jansa et al. The In atoms would occupy the negatively charged Bi vacancies.Thus the Te vacancies would be dominating charged defects in the crystal as In content increases and the conductivity becomes p-type. The explanation as forwarded by Jansa et al however needs an experimental confirmation.

C. Thermoelectric Power Measurement :

The thermoelectric power measurements were carried out on freshly cleaved surfaces of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ single crystals, using Differential Temperature method. The temperature difference between the hot and the cold junctions was kept constant at 5K. The measurements were carried out in the temperature range from 308 to 403 K. The sign of thermal EMF and the results of the hot probe tests show that the $In_{0.1}Bi_{1.9}Te_3$, single crystals are p-type and $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ are n-type in nature, in agreement with the Hall coefficient results. Fig.4 gives the plots of the thermoelectric power versus temperature, obtained for these crystals. The plots indicate that thermoelectic power increases linearly with increasing temperature, agreeing with the behaviour expected of a typical degenerate semiconductor [10].

The thermoelectric power has been used to evaluate the density of charge carrier and the carrier mobility using the relation [11]

$$S = k/e \; [2 + \ln \frac{[2(2\pi m_h^* K_B T)^{3/2}]}{ph^3} \qquad \text{---------(4)}$$

where k = the Boltzmann constant

h = the Planck constant

T = absolute temperature

m_h^*= effective mass of the hole

Using the value of p(n) obtained from Hall measurement and the experimental value of the thermoelectric power at room temperature (308K), the values of m_h^* are calculated with the help of equation (4).

The temperature dependence of the carrier concentration thus obtained for these crystals is shown in Fig.5.

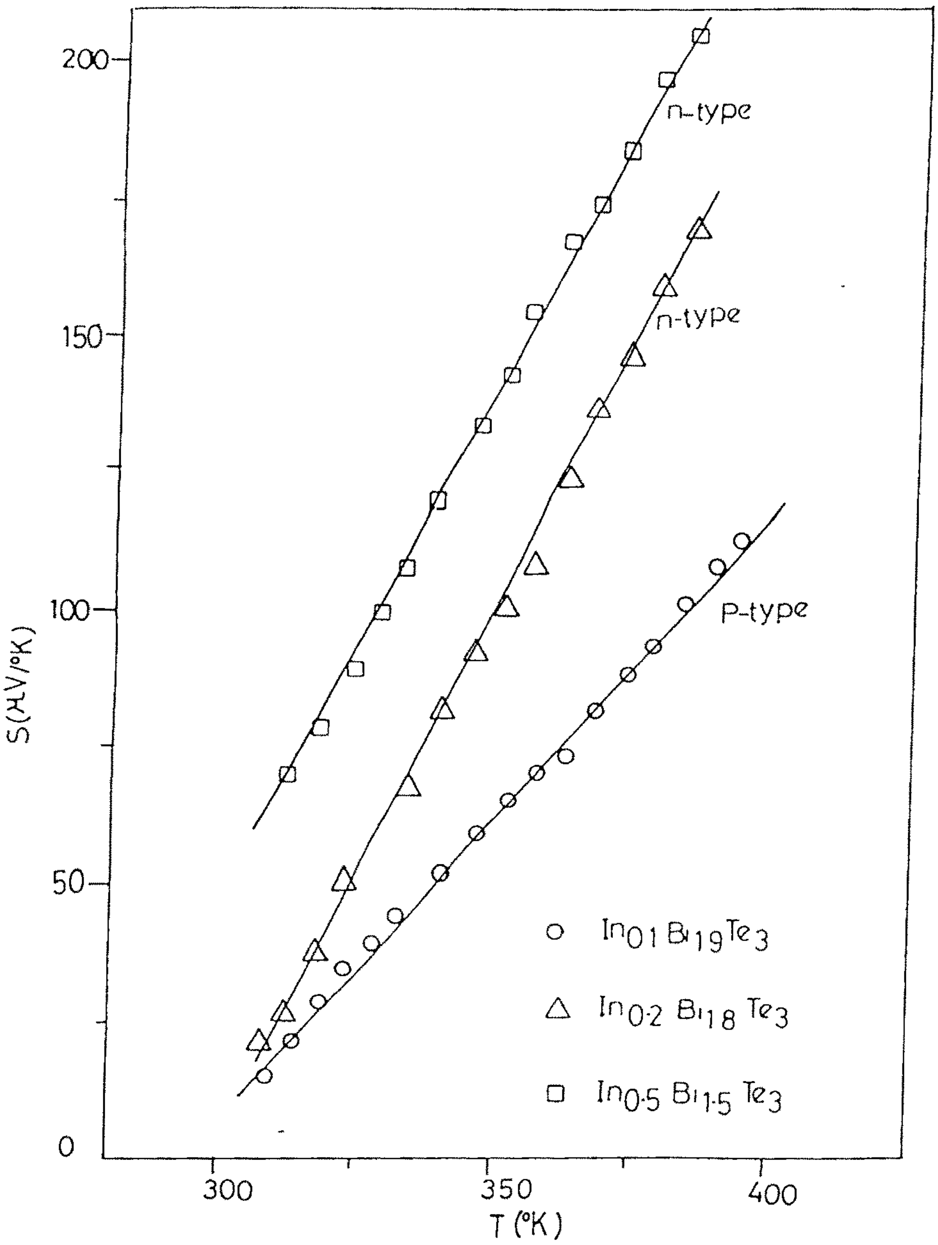

Fig.4. Plots of seeback coefficient (S) vs Temperature (T)

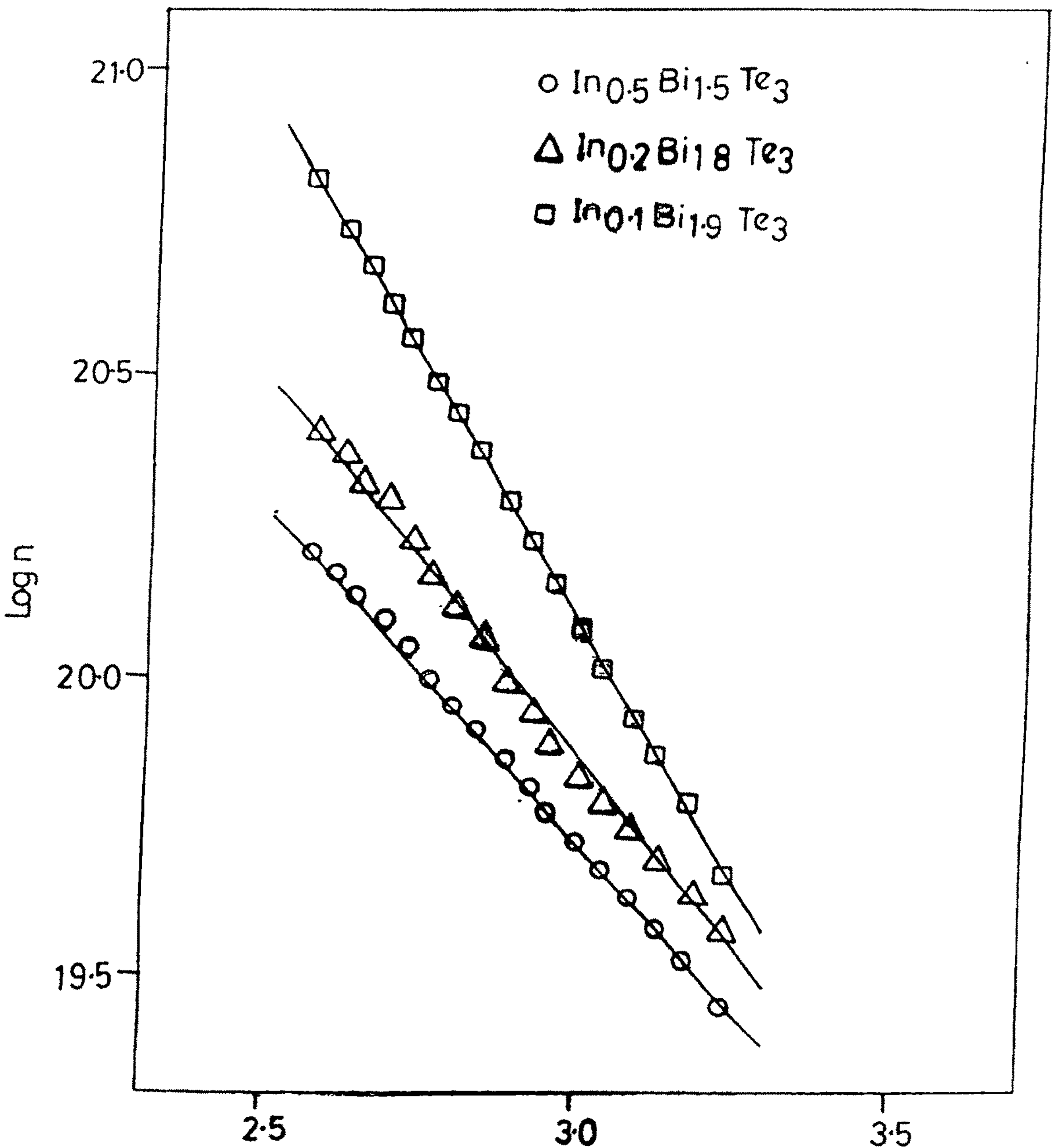

Fig.5. : Plots of Log n vs 1/T

The plots indicate extrinsic conduction in the temperature range 308 to 403 K and obey the relation

$$p(n) \sim \exp [(-Ep/K_BT] \quad \text{-----------------(5)}$$

where $E_{p(n)}$ is carrier activation energy of p(n)- type crystals. The activation energy values evaluated from the corresponding slopes are found to be 0.13eV, 0.098 eV and 0.078 eV for x = 0.1, 0.2, and 0.5, respectively. The low activation energy can be attributed to high carrier concentration ($\sim 10^{19}$ cm^{-3}) giving rise to energy levels very close to the valence band edge.

OPTICAL PROPERTIES:

Optical band gap of the crystals:

The I.R.Spectrophotometer (BOMEM, Canada, MB104) was used for measurement of optical absorption of the samples. In the case of crystals, fine crystalline powder was throughly mixed with spectroscopic grade dry KBr powder at about less than 5% concentration and the mixture was formed into a palette of about 1cm diameter, using vacuum palettizer. The absorption data was used to study the band gap.

Optical band gap of $In_{0.1}$ $Bi_{1.9}$ Te_3, $In_{0.2}$ $Bi_{1.8}$ Te_3 and $In_{0.5}Bi_{1.5}Te_3$ crystals :

The optical absorption was measured in the wave number range 500 cm^{-1} to 4000 cm^{-1} and the absorption spectrum was recorded. By analysing the spectrum, absorption coefficient α was calculated as a function of photon energy. Since in the paletted samples, the material thickness is undetermined an arbitrary thickness was assumed. This would of course not give absolute absorption coefficient. However, the relative variations only are significant for the purpose of evaluating band gap .The plots of $(\alpha h\nu)^2$ vs hν were used to evaluate the optical band gaps. These plots for $In_{0.1} Bi_{1.9} Te_3$, $In_{0.2} Bi_{1.8} Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ are given in Figure-6. The plots are observed to be linear in the region of strong absorption near the fundamental absorption edge. Hence by extrapolating the linear portion to hυ = 0, the band gap was evaluated. The values of the band gaps obtained are given Table-2.As can be seen the energy band gap decreases with increase in In concentraiton. This is consistent with the transition from p-type to n-type conductivity. The acceptor levels nearer the valence band edge (as discussed above) would easily ionize to contribute larger hole concentraion. The band gap narrowing may be unfavorable for the donor levels to ionize or the doner levels themselves would decrease in concentraion as a result of the band gap narrowing.

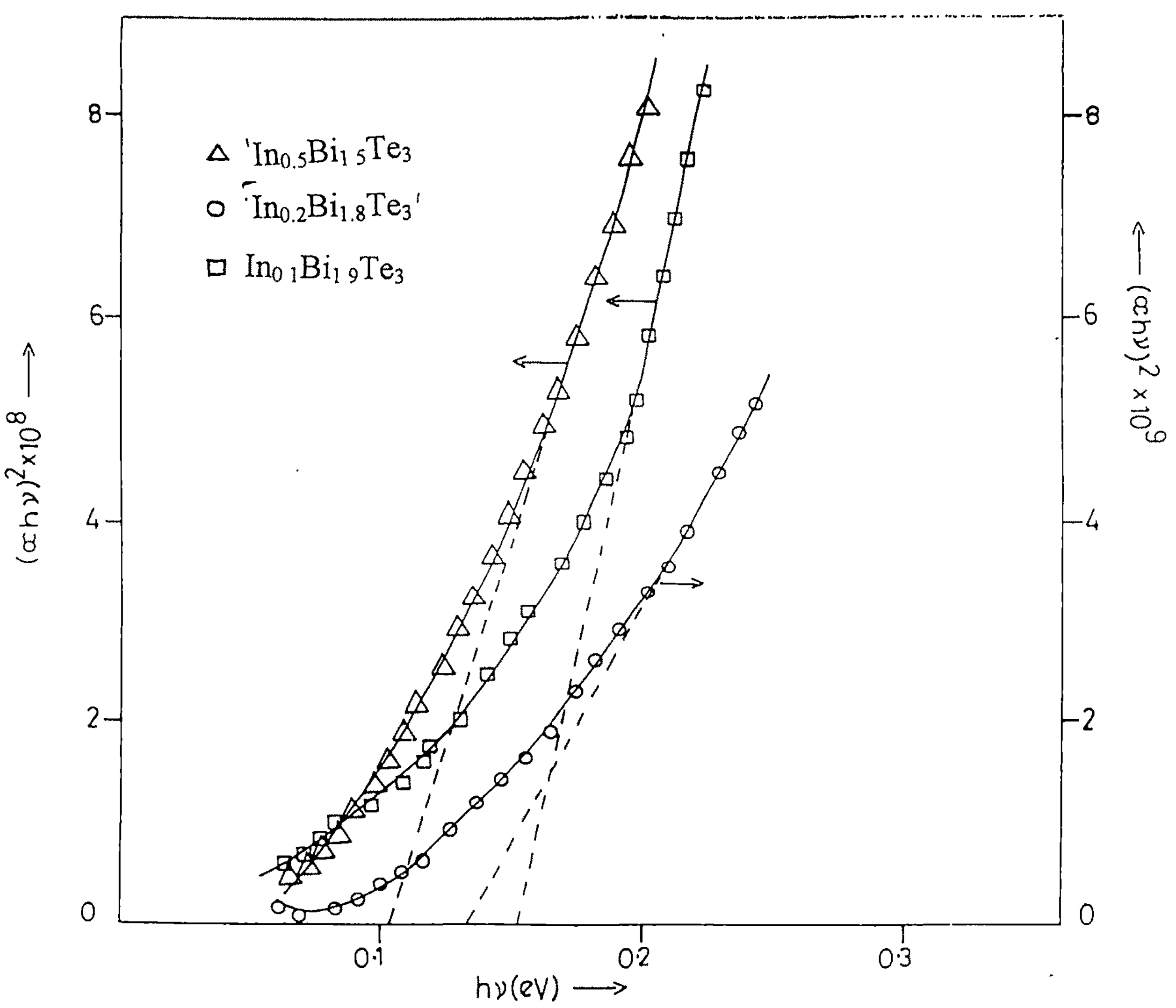

Fig.6.: Plots of $(\alpha h\nu)^2$ vs $h\nu$

Table – 2

Measured Bandgaps

Crystal	Direct gap (eV)
$In_{0.1}Bi_{1.9}Te_3$	0.140
$In_{0.2}Bi_{1.8}Te_3$	0.126
$In_{0.5}Bi_{1.5}Te_3$	0.103

Conclusion:

1. The resistivity activation energy values are found to be 0.015, 0.0198 and 0.028 eV for $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ crystals respectively. To access the intrinsic region, measurement at still higher temperatures need to be conducted.
2. The thermoelectric power in all the crystals increases with temperature.
3. Thermoelectric power measurement indicates $In_{0.1}$ $Bi_{1.9}$ Te_3 crystal to be p-type with carrier concentration 4.78 x 10^{19} cm^{-3} while $In_{0.2}$ $Bi_{1.8}$ Tc_3 and $In_{0.5}Bi_{1.5}Te_3$ crystals are of n-type with carrier concentrations 3.23 x 10^{19} cm^{-3} and 7.57 x 10^{19} cm^{-3}, respectively. The transition from p-type to n-type reported earlier is confirmed.
4. The carrier concentration in these crystals decreases with indium concentration.
5. The optical band gap is found to decrease from 0.14 eV to 0.1 eV with indium concentration varying from 0.1 to 0.5.

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