

**EFFECT OF EXCESS  $B_i$  ON THERMOELECTRIC POWER OF THIN  
FILMS OF  $Bi_xSe_{1-x}$**

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**ABSTRACT**

*Bismuth Selenide has drawn considerable attention due to their thermoelectric properties. In this paper thermoelectric power of polycrystalline thin films of  $Bi_xSe_{1-x}$  were studied in the temperature range from liquid nitrogen to 300K and the effect of excess Bi on it was specifically discussed.*

**1 INTRODUCTION**

Because of the technological importance of  $Bi_xSe_{1-x}$  and its alloys in thermoelectric power conversion [1], its thermoelectric properties have been studied by many workers. Thermoelectric power is an interesting and informative property of a material. Among the various transport properties, thermopower is perhaps the most sensitive to the distortion of the Fermi level. Study of thermoelectric power gives information on the band structure, band parameters and scattering mechanism [2]. In this paper thermoelectric power of  $Bi_xSe_{1-x}$  thin films with different Bi content have been studied with a view to examine its band structure. In section 2, a brief review of thermoelectric power is given. Section 4 deals with the experimental results and conclusions drawn of thermoelectric power on  $Bi_xSe_{1-x}$  samples. The film samples A,B,C and D as a function of absolute temperature (S v/s T) . The variations of thermoelectric power with absolute temperature and having 1%, 2%, 3% and 4% Bismuth have been reported.

**2 THERMOELECTRIC POWER: A BRIEF REVIEW**

Seeback, in 1822, discovered that whenever the ends of two different materials are joined and maintained at different temperatures, an electromotive force (emf) is developed in the circuit.

This effect is known as Seebeck effect [3] and the electromotive force developed is called the Seebeck voltage. For small temperature differences the electromotive force developed is proportional to the temperature difference and depends upon the materials used to form the junction. Let us consider a homogeneous semiconductor sample at the ends of which two identical metallic wires are connected through Ohmic contacts. Let the temperature of the open ends of the metallic wires be  $T_1$  and  $T_2$  and be the temperature at the ends of sample as shown in figure 1. Due to the temperature gradient, a gradient in the Fermi energy, as well as a position dependent electric field is produced. Due to these driving forces (i.e. the electric field, gradient in Fermi energy and the temperature gradient) drift of carriers takes place, which thereby produces a current. The total current is therefore described by following relation [4]

$$J = \sigma \left[ E_x - \left(\frac{1}{e}\right) \left( \frac{\partial E_F}{\partial x} \right) - Q \left( \frac{dT}{dx} \right) \right] \quad (1)$$

where  $E_F$  is the Fermi energy at any point  $x$ ,  $dT/dx$  is the temperature gradient,  $\sigma$  is the conductivity and  $E_x$  is the electric field along the semiconductor sample and metal wires. Current density  $J = 0$  under open circuit conditions, for which electric field obtained as

$$E_x = \frac{1}{e} \frac{\partial E_F}{\partial x} = Q \frac{dT}{dx} \quad (2)$$

This field  $E_x$  gives rise to the potential difference between the ends of the metal wires.

The electromotive force between the ends of the wires is

$$\begin{aligned} V &= - \int_a^d E_L \, dL = \int_a^d - \left[ \frac{1}{e} \frac{\partial E_F}{\partial L} + Q \frac{dT}{dL} \right] dL \\ &= - \left( \frac{1}{e} \right) [E_F(L)]_a^d + \int_a^d Q(T) \left( \frac{dT}{dL} \right) dL \\ &= \int_{T_2}^{T_1} [Q_1(T) - Q_2(T)] dT \end{aligned} \quad (3)$$

where ‘ $Q$ ’ is a function of temperature and  $Q_1$  and  $Q_2$  represent the values of  $Q$  for the semiconductor and the metal respectively. The 1st term in the equation (5.3) is zero because the Fermi level at the points  $a$  and  $d$  is identical.

Thermoelectric power or Seebeck coefficient, with reference to the two materials forming the junctions is defined by the following relation

$$V_{ad} = Q_{ms} / \Delta T \quad (4)$$

In the above relation  $\Delta T = T - T_c$ ,  $Q$  is defined as the relative Seebeck coefficient or thermoelectric power for the intermediate conductors the thermoelectric power between the two materials is the difference between the absolute thermoelectric power of the two materials. Therefore, the thermoelectric power of semiconductors obtained by using junctions between a semiconductor and a metal may be taken to represent the absolute thermoelectric power of a semiconductor, because the thermoelectric power of metals is negligible in comparison to that of the semiconductors. Near the hot junction electrons will acquire more kinetic energy than electrons near the cold junction. The higher energy electrons diffuse from the hot junction towards the cold junction. Because of this depletion of electrons at the hot end an electric potential gradient is set-up, which of course is due to the temperature gradient. Therefore for a given semiconductor [5], the Thermoelectric power is expressed as

$$Q = \frac{\Delta V}{\Delta T} = \frac{\Delta V / \Delta X}{\Delta T / \Delta X} \quad (5)$$

where  $\Delta x$  is the length of the semiconductor over which the temperature differential exists

### 3 MEASUREMENT OF THERMOELECTRIC POWER

Thermoelectric power of given semiconductor [14] is defined as

$$S = \frac{\Delta V}{\Delta T} = \frac{\Delta V / \Delta x}{\Delta T / \Delta x}$$

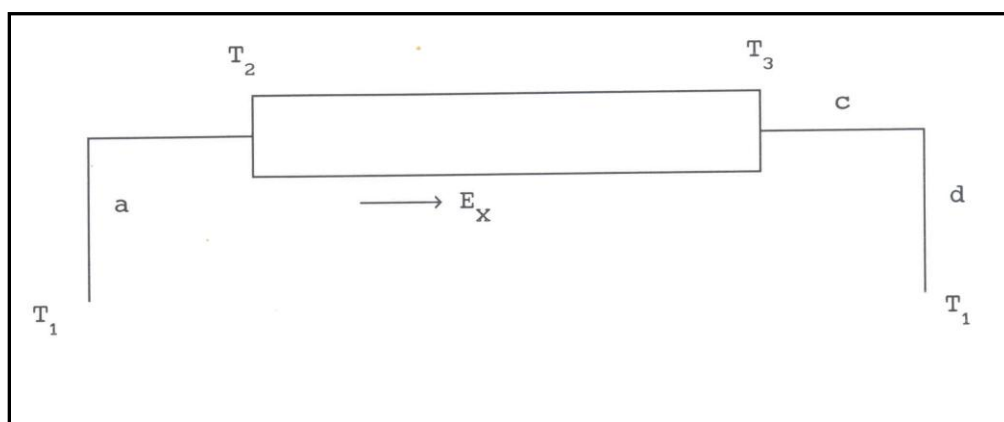
where  $\Delta x$  is the length of semiconductor over which the temperature difference  $\Delta T$  exists.

Thermoelectric power measurements were performed by using a vacuum cryostat shown in fig. 2. A temperature difference was maintained between the two cross-sectional faces of the samples by keeping it on a quartz wedge which in turn was in good thermal contact with the cooled copper block of the cryostat. Temperatures of both ends of the sample were measured with two copper constantan thermocouple soldered with indium at the two ends. The thermal emf so generated was measured with a Philips micro voltmeter. The ohmic natures of the contacts were ensured in the entire temperature range. The temperature dependence of thermoelectric power was determined by maintaining the sample at different temperatures.

If  $V_1$  and  $V_2$  are the two voltages and  $T_1$  and  $T_2$  are the temperature at two ends of the sample therefore,

$$S = \frac{V_2 - V_1}{T_2 - T_1} = \frac{\Delta V}{\Delta T}$$

Hence thermoelectric power is estimated



**Fig.1**

Distribution of temperature in the sample for the experiment of thermoelectric power

The samples were mounted on a copper block (provided with electrical insulation). The copper block was clamped to a sample holder having contact screws insulated from each other. Fine wires (SWG 46) were used and adhered to the contacts with air dry silver paste. The other ends of these wires were connected to the leads through different contact screws. The temperature was measured using a copper- constantan thermocouple. One of thermocouple junctions was soldered to the copper block just below the middle of the sample. The other junction of the thermocouple was kept in liquid nitrogen in a Dewar flask. The copper block was kept in a specially designed vacuum cryostat [13], The cryostat in turn was kept in Dewar flask containing liquid nitrogen as shown in Fig. 2 .The whole system was kept between the pole pieces of an electromagnet capable of giving a magnetic field upto 10 KG. The strength of the magnetic field between the pole pieces was measured with the help of a Hall probe flux-meter

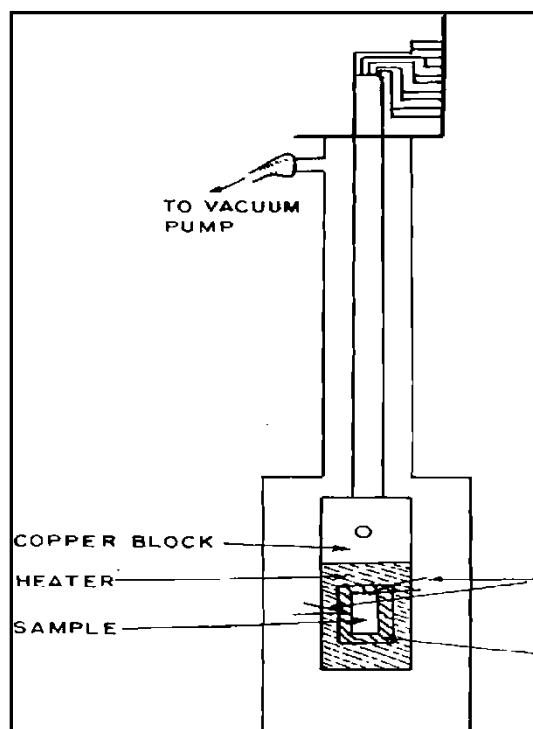


Fig. 2. Schematic diagram of vacuum cryostat (after ref.12).

#### **4 RESULT AND CONCLUSIONS**

The variation of thermoelectric power (S) with temperature (T) for different compositions (A,B,C and D) of  $\text{Bi}_x\text{Se}_{1-x}$  are shown separately in fig. 3 and combined in fig. 4 respectively. It is observed that thermoelectric power is negative throughout the temperature range, for all the samples (A,B,C and D) suggesting that all samples are n type, n-type conductivity maybe due to incorporation of excess selenium in the films [7]. For a given composition of  $\text{Bi}_x\text{Se}_{1-x}$  it is observed that thermoelectric power increases with increasing temperature, attains a maximum value and then decreases with the increase of temperature. This phenomena may be due to the degenerate nature of the material. Same phenomena have been observed by several workers in bulk Bismuth Telluride [8,9] and bulk Bismuth Selenide [10-11]. It is observed that maxima of thermoelectric power decreases with the increase of Bi content for different  $\text{Bi}_x\text{Se}_{1-x}$  composition. It is also observed from the fig. 5.2. that maxima of thermoelectric power v/s temperature variation shifts towards the lower temperature with the increase Bi content in  $\text{Bi}_x\text{Se}_{1-x}$  compositions. The interpretation of these results in that effect of excess Bi is to short the grain boundaries thus reducing the grain boundary barrier potential. This reduction the grain boundary barrier potential is responsible for the decrease in thermoelectric power of  $\text{Bi}_x\text{Se}_{1-x}$  films with increasing content of Bi. These results of thermoelectric power measurement are consistant with the conductivity and Hall mobility data.

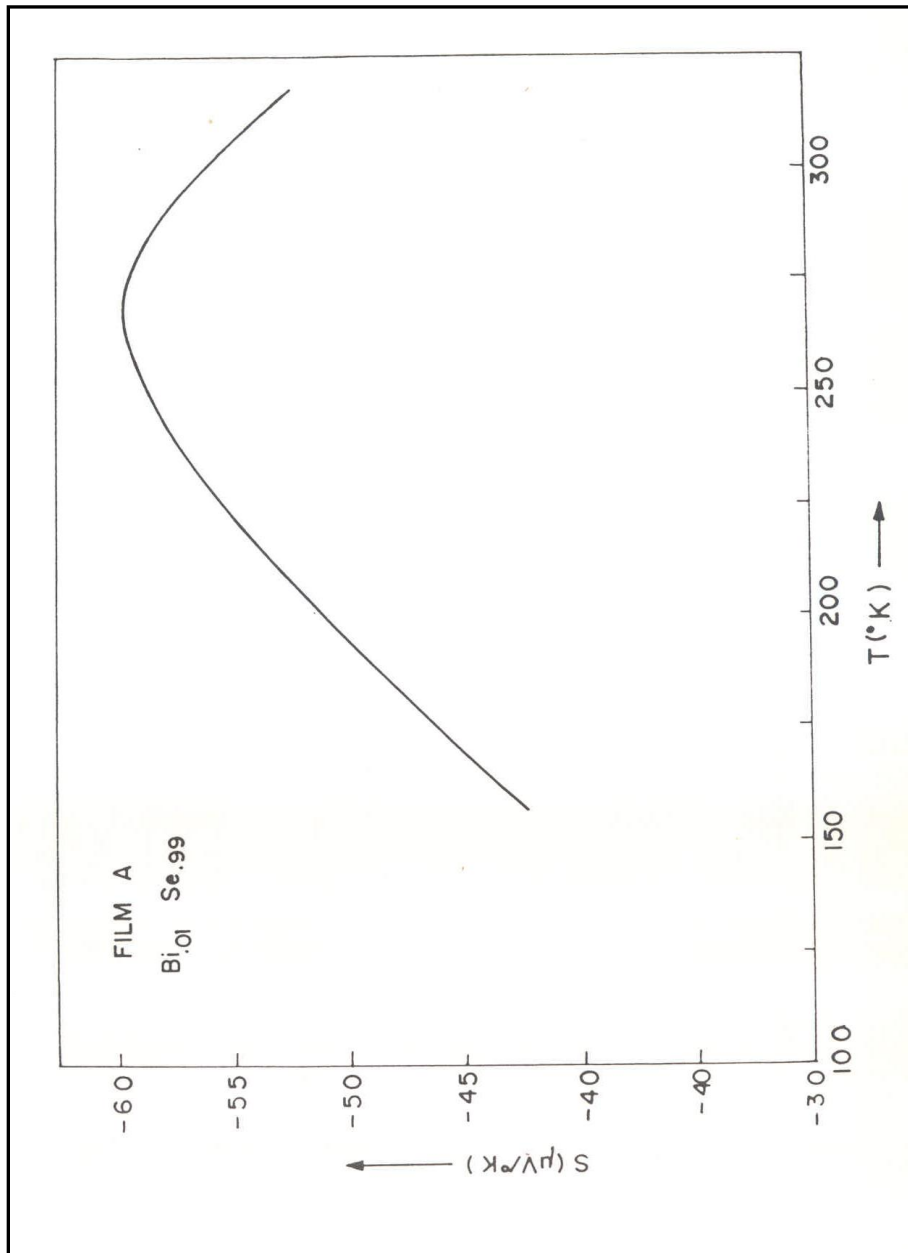


Fig. 3 (a)

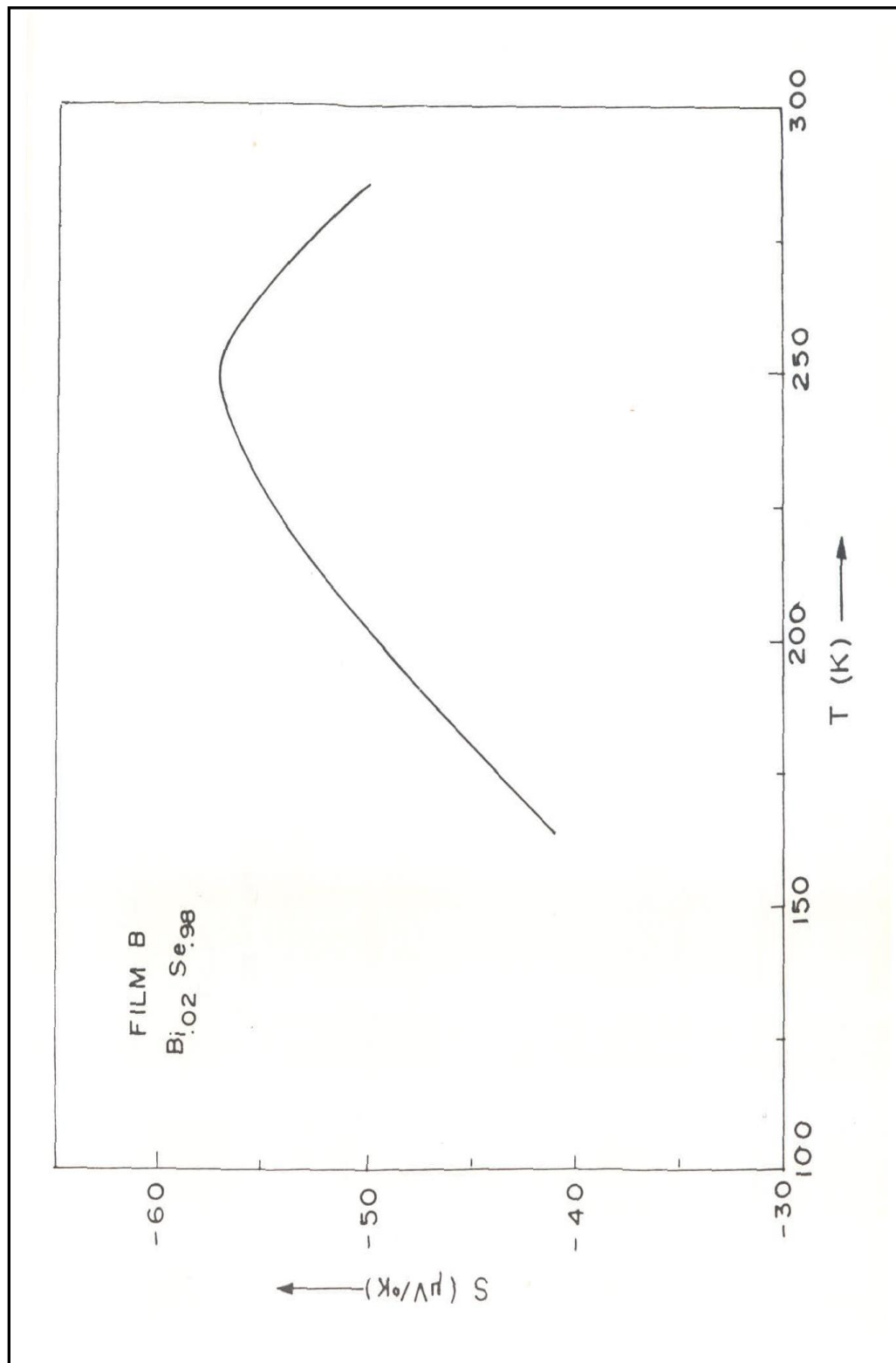


Fig3 (b)



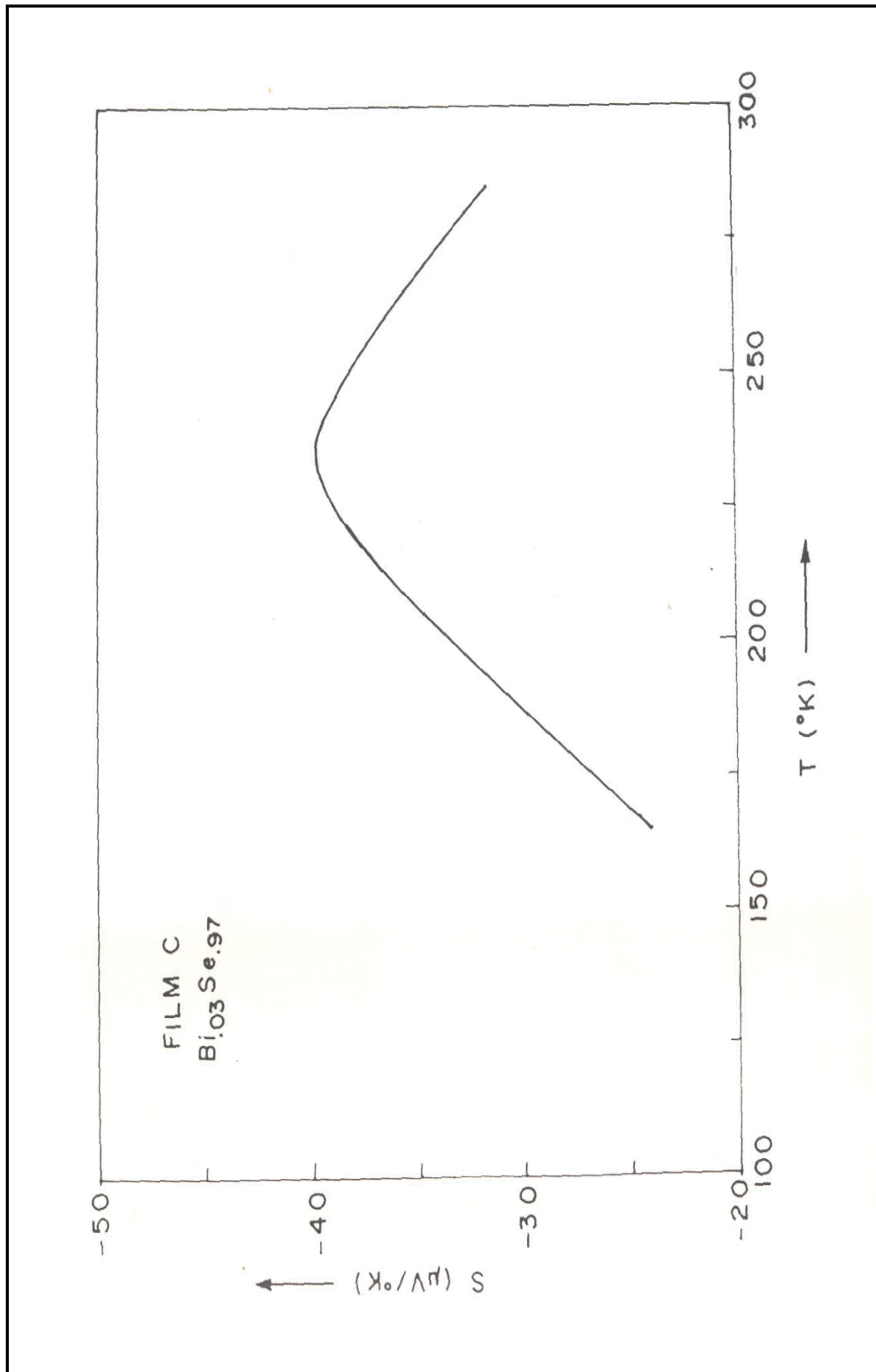


Fig. 3 (c)

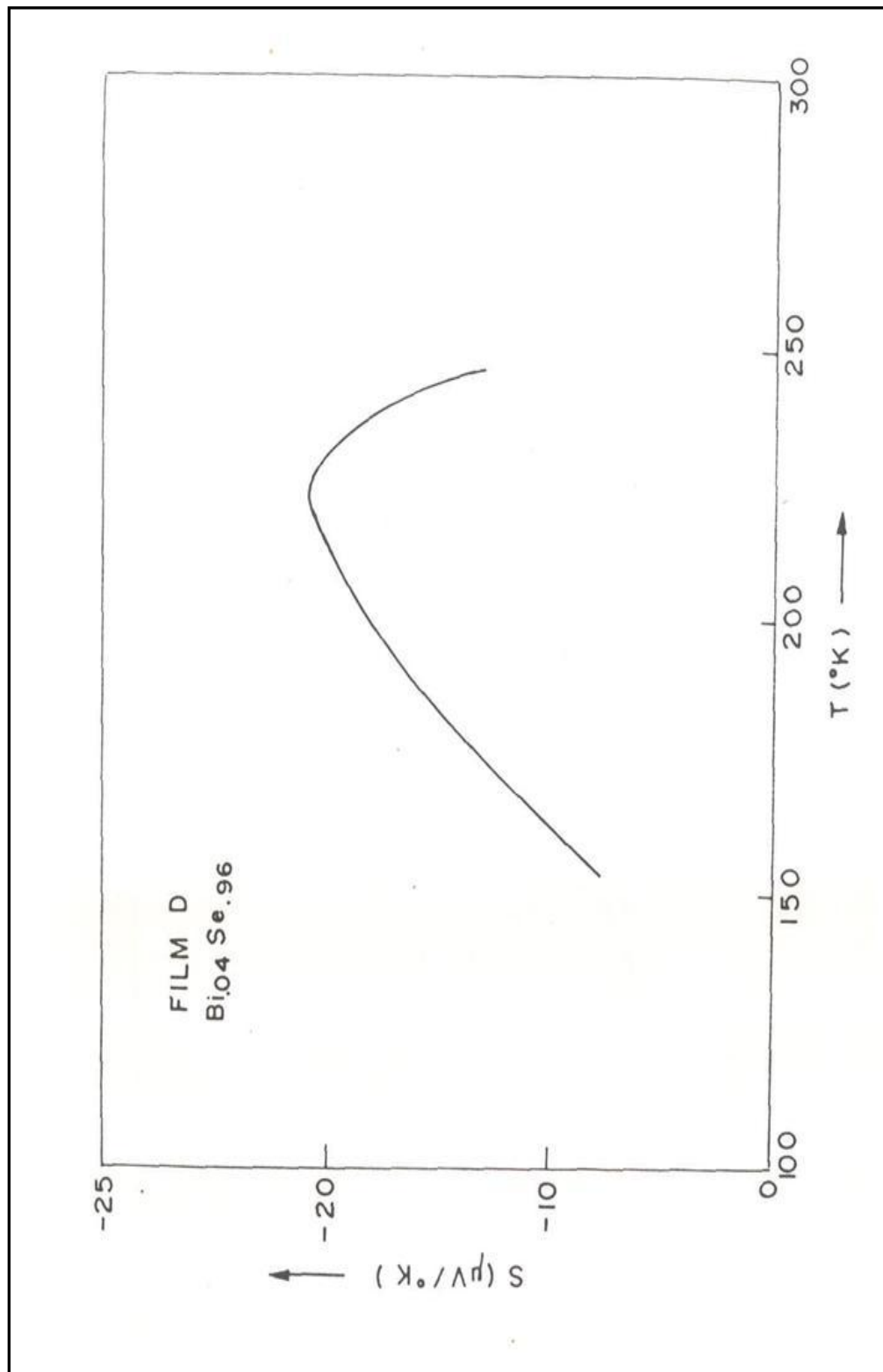


Figure 3(d)

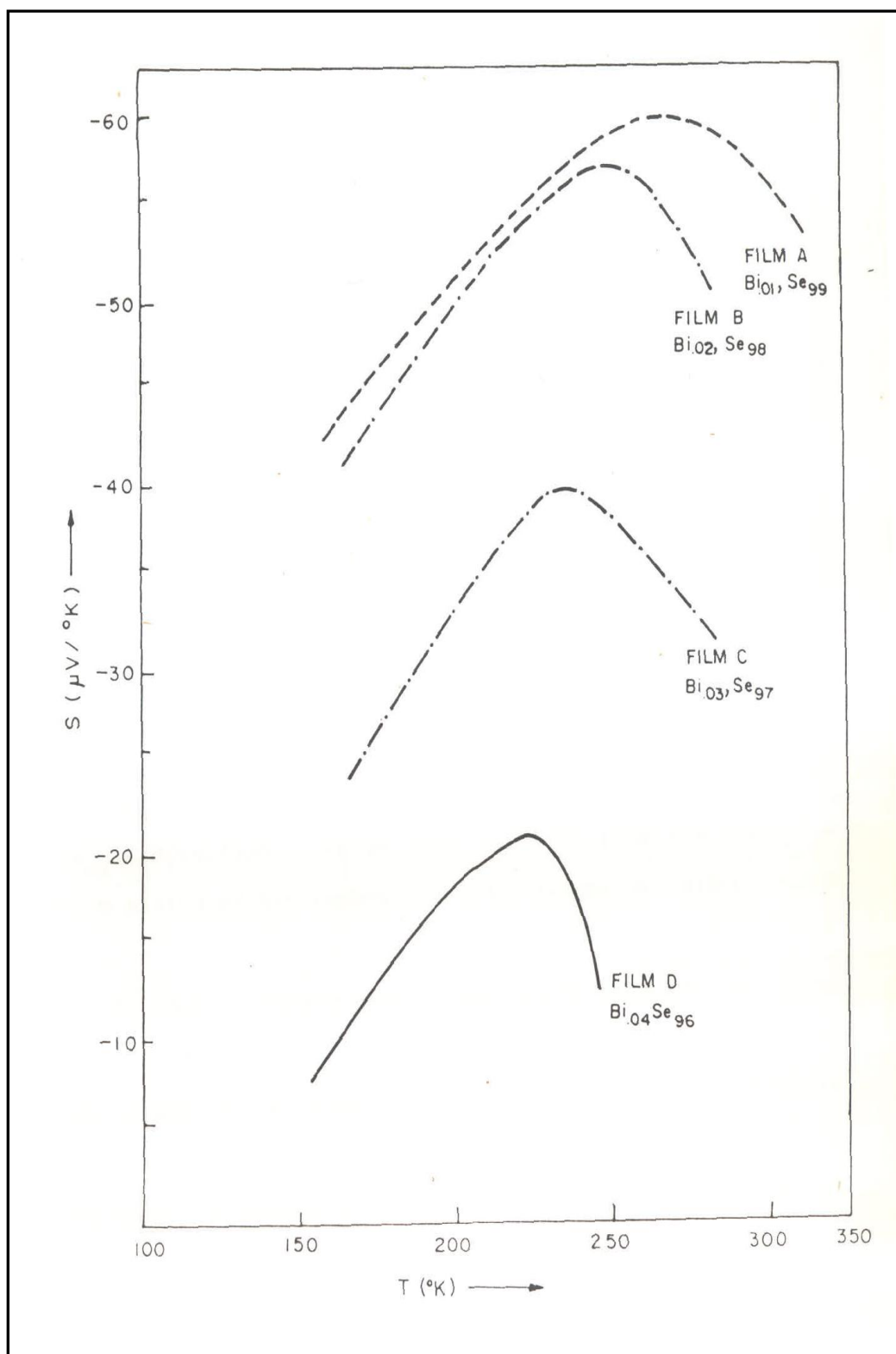


Figure 4

## REFERENCES

1. John, K. (1993). Electrical properties of bismuth selenide thin films. *Solid State Commn*, 85(10), 879-881.
2. Jr., R. (1972). *Semiconductors and Semimetals*. New York: R.K. Willers and sons and A.C. Beer.
3. E.H. Putley. (1960). *The Hall Effect and Semiconductor Physics*. New York: Dover Publications Inc.
4. B.R. Nag. (1980). *Electron Transport in Compound Semiconductors*. Berlin: Springer-Verlag.
5. W.B. Berry, G. a. (n.d.). *Transport properties of solids and solid state energy conversion*. Bombay-New Delhi: Tata McGraw Hill Publishing Company.
6. P.B. Kireev. (1974). *Semiconductor Physics*. Moscow: Mir Publishers.
7. K.G. Gunther, W. a. (1959). In *Naturewissenschaften* (Vol. 46, p. 319).
8. H.J. Goldsmid. (1958). *Proc. Phy. Soc*, 71, 633. LONDON.
9. J. Black, E. a. (1957). *J. Phy. Chem. Solids*, 2, 240.
10. G.R. Hyde, H. a. (1972). *Phy. Lett A*, 41A, 319.
11. A.A. Sher, I. a. (1984). *Inog Mater*, 20, 1109.
12. G. Sauerbrey, A. (1964). *Electrotech Ubertragung*, 18, 617.
13. Shashi Bala (1984), Ph.D. Thesis, University of Delhi.
14. B.R. Nag. (1980). *Electron Transport in Compound Semiconductors*. Berlin: Springer-Verlag.
15. E.H. Putley. (1960). *The Hall Effect and Semiconductor Physics*. New York: Dover Publications Inc.
16. G.R. Hyde, H. a. (1972). *Phy. Lett A*, 41A, 319.
17. G. Sauerbrey, A. (1964). *Electrotech Ubertragung*, 18, 617.
18. H.J. Goldsmid. (1958). *Proc. Phy. Soc*, 71, 633. LONDON.
19. J. Black, E. a. (1957). *J. Phy. Chem. Solids*, 2, 240.

20. John, K. (1993). Electrical properties of bismuth selenide thin films. *Solid State Commn*, 85(10), 879-881.
21. Jr., R. (1972). *Semiconductors and Semimetals*. New York: R.K. Willers and sons and A.C. Beer.
22. K.G. Gunther, W. a. (1959). In *Naturewissenschaften* (Vol. 46, p. 319).
23. P.B. Kireev. (1974). *Semiconductor Physics*. Moscow: Mir Publishers.
24. W.B. Berry, G. a. (n.d.). *Transport properties of solids and solid state energy conversion*. Bombay-New Delhi: Tata McGraw Hill Publishing Company.
25. Shashi Bala (1984), Ph.D. Thesis, University of Delhi