# CHAPTER: 1

# INTRODUCTION

Metals and dielectrics are the two major groups of materials, which were in focus for physicists and electric industries during last two centuries. There have been numerous advances in both materials science and materials technology that have exerted a considerable impact on the development of new materials and improvement of existing materials. The main support has come from the newer technologies associated with missiles and space research, high speed flights, nuclear engineering, computer, electronics and control engineering. From these fields have come demands for new materials to withstand condition not previously envisaged. At this juncture it was realized that a new basic and fundamental approach to material have bridged the gulf between the two extreme group of metals and insulators and have found diverse technical applications.

The best known semiconductor is undoubtedly silicon (Si). In addition many minerals found in nature, such as zinc-blends (ZnS), cuprite ($Cu_2o$) and galena (PbS) to name a few are semiconductors. The family of semiconductors, including those synthesized in laboratory, forms one of the most versatile class of materials known to man. Si and Ge together are the prototypes of a large class of semiconductors having similar structures. Compounds formed from elements of the group III and V of the periodic table, such as GaAs, have properties very similar to their group IV counterparts. In going from the group IV elements to the III-V compounds, the bonding becomes partly ionic due to transfer of electronic charge from the group III atom to the group V atom. The iconicity becomes even larger and more important in the II-VI compounds such as ZnS. As a result, most of the II-VI compound semiconductors have band gaps larger than 1eV (except HgTe) and find potential applications for displays and lasers. The semiconductors with smaller band gaps among these are important materials for the fabrication of infrared detectors. Binary compounds formed from group IV and VI elements, such as PbS, PbTe and SnS are narrow gap semiconductors like HgTe in spite of their large ionicity. These small band gap IV-VI semiconductors are important infrared materials and can work as thermal detectors. On the other hand, the V-VI compounds like $Bi_2Te_3$, $Sb_2Te_3$ and $Bi_2Se_3$ which also possess narrow band gaps display interesting thermoelectric properties.

## THERMOELECTRICS

The materials chosen for the presently study belong to the last group of semiconductors mentioned above. In view of this, it is noteworthy that in recent years a significant part of the nation’s total research and development efforts 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. Some of the current and proposed applications for thermoelectric devices appear in Table. 1[1].

Thermoelectric cooling devices are solid-state modules whose operations are inverse to those of thermocouples and function on the well-known principle of the Peltier effect. Miniature thermoelectric  cooler (TE) are now finding widespread use in the field of optoelectronics for controlling and tuning the performance of various optoelectronic devices such as lasers and detectors, through precise temperature control[2] and cooling[3]  with improved design and fabrication technologies resulting in better performance efficiencies of TE coolers, their use for cooling critical components is steadily increasing . Thermoelectric cooling devices are very reliable, having no moving parts, no liquid, no gases and no compressor.

TABLE 1

Current and Proposed Applications for Thermoelectric devices

REFRIGERATION

Spot Cooling of Electronics

- Infrared detectors
- Computer central processing units
- X-ray detectors
- Fiber-optic laser packages

Picnic Coolers (Powered by Car Battery)

Air conditioning in Submarines and Railway Coaches

Water Coolers

Superconducting Electronics

| |
|---|
| Home Refrigerators |
| POWER GENERATION<br>Power for Deep-Space Probes ( Pioneer, Viking, Voyager, Galileo )<br>Remote Weather Stations<br>Remote Navigational Systems<br>Submarines<br>Subsea Power Generation( for Petroleum Wellhead Valves )<br>Conversion of Waste Heat into Useful Electrical Power<br>• Large diesel trucks<br>• Steel industry<br>• Chemical industry |

An important factor in their favour is that the coefficient of performance is independent of the system size. This leads to fabrication of miniature low-capacity cooling devices, which are found in a variety of commercial industrial, medical and laboratory appliances. However, if we go back to the past when thermoelectric effect was first observed by seebeck in 1822, the only devices employed until mid twentieth century were metallic thermocouples for the measurement of temperature and thermopiles for the detection of radiant energy (based on the principle of thermoelectric generation of electricity from heat). The thermoelectric refrigerator using the Peltier effect was impossible then. The lack of practical applications of thermoelectricity then had resulted from the low thermoelectric efficiency of known materials.

The thermoelectric efficiency of a material depends on the thermoelectric figure of merit (Z) defined by [4]

$Z=\alpha^2\sigma / \kappa$

Where α is Seebeck coefficient, σ is electrical conductivity, and κ is thermal conductivity.

The basic theory of thermoelectric generator and refrigerators was first derived satisfactorily by Altenkirch in 1909 and 1911. He showed that for both the applications, materials were required with high thermoelectric coefficients and electrical conductivities to minimize Joule heating and low thermal conductivities to reduce heat transfer losses.

The Wiedeman-Franz law states that the ratio of the thermal to electrical conductivities is the same for all metals at a given temperature. The maximum values of the figure of merit for metals are therefore obtained when the Seebeck coefficient is highest. However in no metallic thermocouple can a differential Seebeck coefficient of more than 100 $\mu V/^0C$ be realized. Hence no real progress was made with metallic thermocouples. It is only since semiconductor thermocouples have been prepared that efficient thermoelectric generators and refrigerators have become possible. In semiconductors, absolute Seebeck coefficients of up to one or more millivolts per degree may be obtained, but it is generally found that the ratio of thermal to electrical conductivity is much higher than the value given by the Wiedemann-Franz law. It is thus not immediately obvious that semiconductors are superior to metals as thermoelectric materials.

However, it has been found that higher values of Z may be obtained with some semiconductors than for any metals.

The maximum value of Z which can be achieved using metals or metallic alloys was 0.23 x $10^{-3}$ $K^{-1}$, viz, that of Bi-Sb couple using 91%Bi and 9%Sb. Insead of pure Bi as the negative thermo element. The thermocouple having the highest figure of merit, prior to 1950 as described by M. Telkes [36]. She found that the best positive thermoelectric material was ZnSb and when the compound contained small quantities of Sn and Ag, its Seebeck coefficient measured against constantan was found to be 250 µ $V^0C^{-1}$. The maximum figure of merit Z for ZnSb is about $10^{-30}K^{-1}$but the overall value of Z for a ZnSb-constantan thermocouple is only 5x$10^{-40}K^{-1}$. There has been considerable improvement in thermoelectric materials since Telkes published the result of her survey. These improvements have come about largely owing to the use of compounds composed of elements of high atomic weight.

# General information about $Bi_2Te_3$

The studies of Ioffe [4] demonstrated that the most promising materials for thermo-electric applications were compound semiconductors resulting from the compounding of elements from groups$II_{\boldsymbol{B}} - V_B$,$IV_{\boldsymbol{A}} - VI_A$, and $V_{\boldsymbol{A}} - VI_A$ of the periodic table. Established on the large number of possibilities suggested by early workers, an exploratory research on thermo electric refrigeration was begun at many laboratories in the early 1950's. The highest figure of merit has been achieved using either the compound of lead with group VI elements or V-VI group compounds. Lindenblad[5] of RCA Laboratories constructed a small experimental thermoelectric refrigerator in 1954 using n-type lead telluride and p-type antimony telluride; and thus opened the way for his subsequent construction of a 4-ft$^3$ refrigerator (using both n- and p- type bismuth tellurides). This was the first demonstration of a large-scale thermoelectric refrigerator.

Among the first and perhaps the most important works that established $Bi_2Te_3$ as a material of great promise for Peltier cooling was the investigation by Goldsmid and Douglas published in 1954[6]. Today, this compound semiconductor remains one of the major constituents in the best thermoelectric materials for use near room temperature. Equally significant in the development of useful thermoelectric materials is the concept of solid solution alloying first proposed by Ioffe and his co-workers [7]. Their theoretical considerations suggested that solid solution alloying can improve the thermoelectric figure of merit by decreasing the lattice thermal conductivity without adversely affecting the electrical properties.

This is because alloying introduces short-range distortions in the lattice, which greatly enhance scattering of phonons but are much less effective in scattering charge carries that have longer wavelength than phonons. This concept led to considerable research in recent years on the thermoelectric properties of alloys of compound semiconductors, particularly alloys in the generalized system $(Bi, Sb)_2Te_3$[8-11]. Important in this connection is the work of Berkholz[8], and Rosi, Abeles and Jensen[9] who showed a significant reduction in the lattice thermal conductivity of $Bi_2Te_3$ upon alloying with $Sb_2Te_3$ or $Bi_2Se_3$. Bismuth telluride and Antimony telluride, which have the same rhombohedral structure, form a continuous series of solid solutions [12]. Undoped $Bi_2Te_3$- $Sb_2Te_3$ alloys are all p-type and the hole concentration increases markedly toward the $Sb_2Te_3$ rich region. Because of this strong p-type characteristics, studies to optimize the figure of merit of these alloys were confined to p-type materials. Carrier concentrations can be adjusted by controlled addition of doping materials. Elements, such as those in Groups $IV_A$ and $V_A$ (Sn, Pb, As, Sb and Bi), as well as Cd, were all found to provide free holes in $Bi_2Te_3$ were obtained with additions of excess Bi[9] or Pb[11].

The $V_2$-$VI_3$ (V = Bi, Sb; VI = Se, Te) binary compounds and their pseudobinary solid solutions are known to find applications ranging from photoconductive targets in T.V. cameras to I.R.Specroscopy [13]. These compounds have band gaps: $E_g$~ 0.2eV, ~0.35 eV and ~0.16 eV for $Sb_2Te_3$, $Bi_2Se_3$, and $Bi_2Te_3$, respectively. There are also a few applications for temperature control of Laser diodes [14], optical recording system [15] and strain gauges [16]. Among these $Bi_2Te_3$ is the most potential material for thermoelectric device such as thermoelectric generators, thermocouples, thermo coolers, and I.R.Sensors with the best figure of merit near room temperature [14,17-20,33]. $Bi_2Te_3$ finds applications also in electronic, microelectronic, optoelectronic and electrochemical devices [21-22]. There have been various studies on the optical and electrical properties of single crystals and thin film of $Bi_2Te_3$ [23-26]. Its single crystals can be grown by vapour phase technique [13]. They have also been grown by Bridgman-Stockbarger method and Zone melting method [22]. There is also a report on micro hardness of $Bi_2Te_3$ single crystals [13].

Its melting point is 573˚C and its density, 7.7 gm/cc[27]. $Bi_2Te_3$ and its pseudo binary compounds are highly anisotropic and crystallize into homologous layered structures parallel to the c-axis [28]. The basic unit cell is rhombohedral, but a hexagonal unit cell is often used in its crystal-structure studies. We have used rhombohedral coordinate system for identifying the crystallographic planes [22]. Bismuth telluride possesses the symmetry elements:

a) The three-fold rotation axis [111]
b) Three reflection planes containing the three-fold axes
c) Three two-fold (binary) axes $[1\bar{0}1]$, $[\bar{1}10]$ and $[0\bar{1}1]$, normal to the three fold axis and bisecting the angle between the reflection planes; and
d) A centre of symmetry.

The plane normal to the three fold rotation axis [the (111) plane] is also the cleavage plane and is sometimes identified as the c-plane. $Bi_2Te_3$ has the space group $R\bar{3}m$[22] with lattice parameters: a= 4.3852 Ȧ, c = 30.483 Ȧ giving c/a = 6.9513[29].

It is a p-type semiconductor and has a direct band gap of 0.16 eV. At room temperature, the thermoelectric power perpendicular to the c-axis is 218 µV/K [18]. Its electrical resistivity is of the order of $1.6\times10^{-5}$ ohm.m[30]. At room temperature, the Hall coefficient and carrier concentration are $0.42\times10^{-6}$ $m^3$/A.sec. and $1.75 \times 10^{25}$ $m^{-3}$, respectively [30-31]. Its Vickers microhardness is about 448 MPa. Electrical conductivity and thermoelectric power of its thin films increase with thickness and attain constant values of $0.3\times10^{5}$ $ohm^{-1}$ and 200μV/K, respectively, at the thickness of ~ 2000 A[32]. The thickness dependence has been explained in terms of the size effect. The absolute value of TCR and resistivity activation energy are $40\times 10^{-4}$ °C and 0.0287 eV, respectively, at room temperature[32].

$Bi_2Te_3$ has the rhombohedral crystalline structure of the space group $R\bar{3}m$ with five atoms in one unit cell (Fig. 1.1). [35]. The structure of this compound is shown in (Fig. 1.2). [34]. Fig. 1.3 shows that the phase diagram of $Bi_2Te_3$ compound[35].

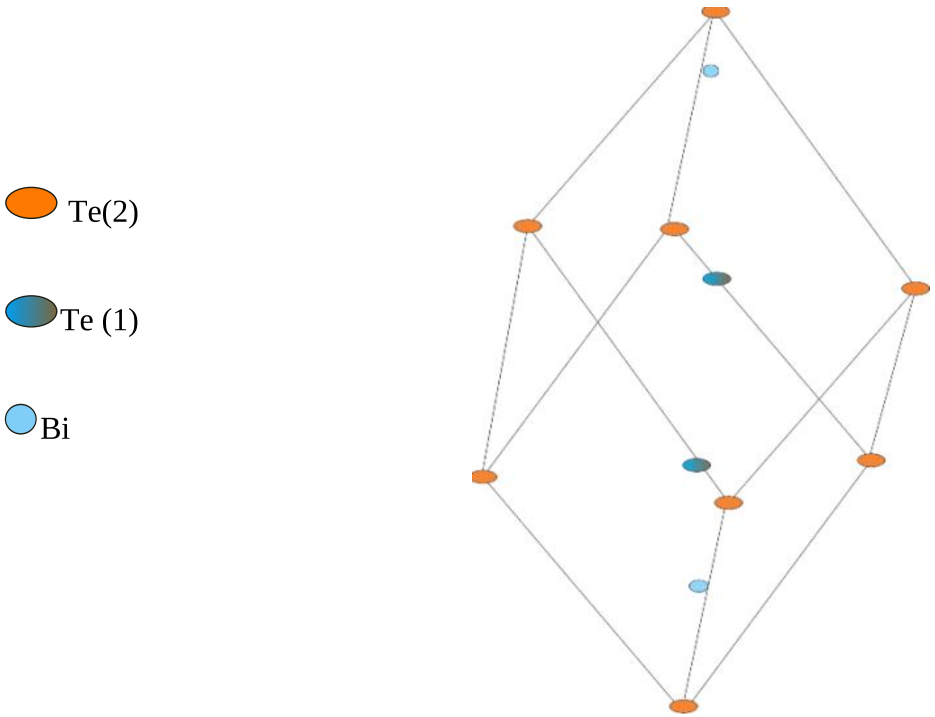

Fig.1.1 Rhombohedral elementary unit cell.

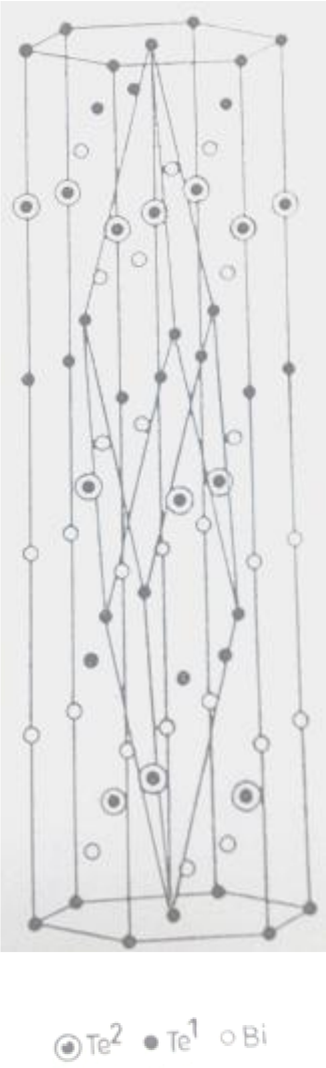

Fig.1.2 Crystal structure of the compound $Bi_2Te_3$.

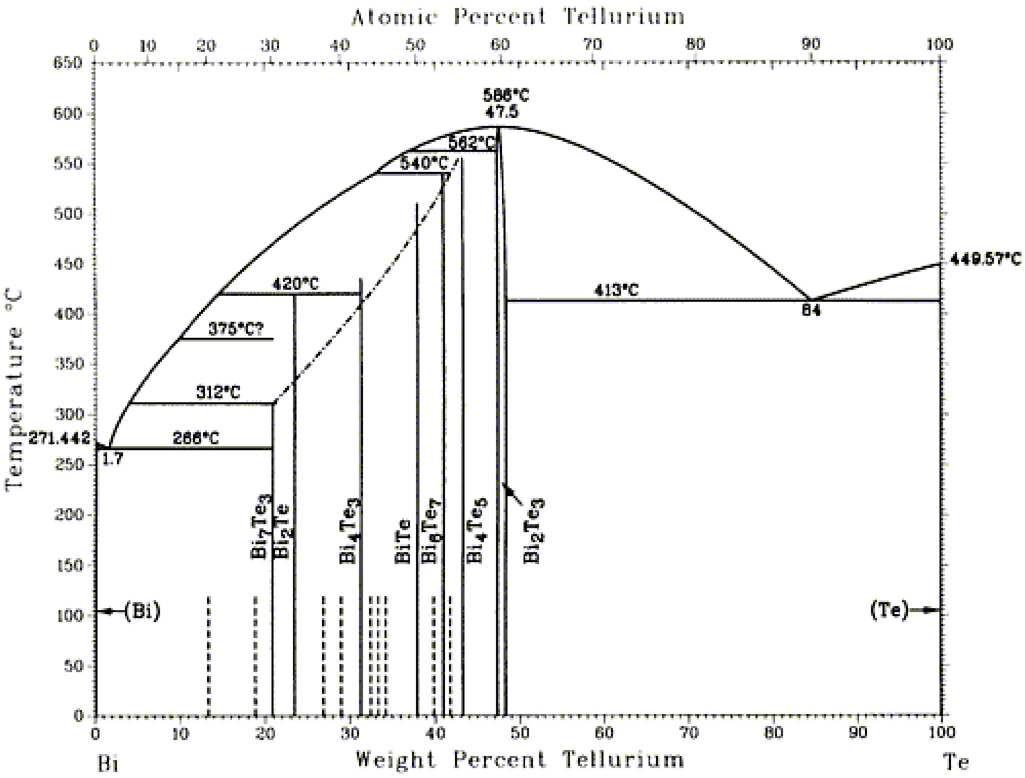

Fig.1.3 Phase diagram of the compound Bi-Te

## THE PRESENT STUDY

Looking into the different perspectives of the studies that have been carried out on $Bi_2Te_3$ system and their wide scope applications, the purpose of the present study is to explore a new aspect of this problem on $Bi_2Te_3$ crystals, namely, doping effect of Sb on $Bi_2Te_3$. A systematic study on the crystal growth, compositional, structural characterization, micro hardness and optical band gap of these crystals has been carried out. Further, thin film study of optical band gap has been carried out on the $Bi_{2-x}Sb_xTe_3$ quasi ternary system. The different techniques used and the results of the investigations are given in the chapters that follow.

## REFERENCES:

1. Sales, B. C. (1998) MRS Bulletin, 23 (1), 16.
2. Rowe, D. M. and Bhandari, C.M. (1983) Modern Thermoelectrics, Holt, Rinchart, and Winston, London, 103
3. “A New Generation of Cooling Devices” (1995) Photonic Spectra, 50
4. Ioffe. A. F. (1957) Semiconductor Thermo elements and Thermoelectric Cooling, Info search, London.
5. Lindenblad, N.E. (1954) Unpublished results.
6. Goldsmid, H. J.; Douglas, R. W. Thermoelectric. Br. J. Appl. Phys.1954, 5, 458.
7. Ioffe, A.F., Airapetiants, S.V., Ioffe, A.F., Kolomets, N.V. and Stil’bans, L.S. (1956) Dokl. Akad. Nauk. SSSR 106,981.
8. Birkholz, U. (1958) Z.Naturforsch, 13a, 780.
9. Rosi, F.D., Abeles, B. and Jensen R.V. (1959) J.Phys. Chem. Solids 10, 191.
10. Smirous, K. and Stourac, L. (1959) Z.Naturforsch, 14a, 848.
11. Rosi, F.D., Hockings E.F. and Lindenblad, N.E. (1961) RCA Rev.22, 82.
12. Smith, M. J., Knight, R.J. and Spencer, C.W. (1962) J. Appl. Phys. 33, 2186.
13. Arivuoli D., Gnanam F. D., Ramasamy P., J. Mater. Sci. Letters 7 (1988) 711.
14. Rowe D. M. and Bhandari C. M., Modern Thermo electrics, (Holt, rinehort and Winston, London, 1981) p.103.

15. Watanbe K., Sato N. and Miyaoka, J. Appl. Phys. 54 (1983)1256.

16. Atkulov Sh. B., Azimov T. and Shamisiddinov A. N., Sov. Phys. Semicond. 16(1982)1326.

17. Goodman C.H.L., Mater. Res. Bull., 20(1985)237.

18. Jansa L., Lostak P., Sramkova J.and Horak J., J. Mater. Sci., 27(1992) 6062.

19. Roy B., Chakraborty B. R. and Dutta A. K., Solid State Commun, 25(1978) 937.

20. Jeon H. W., Ha H. P., Hyun D. B. and Shim J. D., J. Phys. Chem. Solids, 52(1981)579.

21. Sakai N., Kajiwara T., Takemura K., Minomuara S., and Fuji Y., Solid State Commun., 40(1981)1045.

22. Sagar A., Faust Jr. J. W., J. Appl. Phy., 38(1967)482.

23. George J. and Pradeep B., Solid State Commun. 56(1985)117.

24. Rahmankhan M. S. and khtaurzzaman M. A., Ind. J. Pure and Appl. Phys., 20(1982)656.

25. Testardi L. R. and Borstein E., Physical Review B, 6(1972)460.

26. Guha S. R., Thakurta and Bose A. K., Ind. J. of Phys., 44(1970)601.

27. Handbook of Chemistry and Physics, 45th ed., eds. R. C. Weas, S. M. Belby and C. D. Hodgman, Pub.: The Chemical Rubber Co. Cleveland, Ohio, (1964) B – 157.

28. Stolzerm M., Stordeur M., Sobotta H.and Riede V., Phy. Stat. Sol. (b), 138(1986)259.

29. JCPDS (File) ed. 1982, pub: International Center for diffraction data, Pennsylvania-19081, U.S.A., Vol. 15-863.

30. Faust J. W., Jr. Recent Newspaper, Ottawa Meeting, Electrochemical Society, October 1958.

31. Kutasov V. A., and luk'yanova L.N., Sov. Phys. Solid State (U.S.A.) 283(1986)502.

32. Horak, J., Strg, Z, and Klikorka, J. Phys. Status Solidi B (East Germany), 147, 2(1988)501.

33. Kokh K. A., Makarenko S. V., Golyashov V. A., Shegaid O. A. and O. E. Tereshchenko , Cryst. Engg. Comm., 2014, 16,581

34. Mishra S K, Satpathy S and Jepsen O., *J. Phys.: Condens. Matter*,1997 **9** 461

35. Handbook of Chemistry and Physics, 93rd Edition, William M. Haynes (2012).

36. Telkes M., J Appl. Phys. 18(1947)1116.