Chapter 3

CRYSTAL GROWTH OF $Bi_{2-x}Sb_XTe_3$ SINGLE CRYSTAL

Crystal growth concepts have been fundamental to many areas of science for quite some time. Disciplinesas diverse as mineralogy, meteorology, biology, medical science, astrophysics and chemical engineering have contributed to and benefitted from the crystal growth concepts. It was, however, not before the onset of the materials science era and the mushrooming development of the electronic and optical materials industries that crystal growth began to develop into a discipline in its own right. In concerted efforts, solid-state physics and crystal growth research has led to many new materials and devices. Their applications have had a great impact on modern life. Today crystal growth forms one of the main pillars of modern technology.

To grow a good crystal is an artistic science. The growth techniques involve an immense arsenal of laboratory methods ranging from ultra-high vacuum to ultra-high pressures and from cryogenics to plasma temperatures. The success of a technique in obtaining good large crystals depends on various factors:

The success of a technique in obtaining good large crystals depends on various factors:

- nature of material itself
- its purity
- thermal environment
- growth rate

- pressure
- diffusion coefficients of the materials
- impurity concentration
- homogeneity

Classification of system for better growth of crystal is shown Table.1 by Laudise[1].

Table – 1

Crystal growth methods

Monocomponent	Polycomponent
A Solid –solid (solid growth) 1. strain annealing 2. Diversification 3.Polymorphic-phase change	A Solid-solid (solid growth) 1. precipitation from solid solution

B Liquid-Solid (melt growth)	B Liquid-Solid (melt growth)
1. Conservative (a) Directional solidification (Bridman-Stockbarger) (b) Cooled seed (Kyropouls) (c) Pulling (Czochralski) 2. Non conservative (a) Zoning (horizontal, vertical float zone, growth on a pedestal) (b) Verneuil (Flame fusion, plasma, arc image)	1. Growth from solution (evaporation, slow cooling, and temperature differential) ▪ aqueous solvents ▪ organic solvent ▪ molten-salt solvent ▪ solvents under hydrothermal condition ▪ other organic solvents 2. Growth by reaction (media as above temperature change, concentration change) ▪ chemical reaction electrochemical reaction

Thus, as shown in table, crystals can be grown from the solid, liquid or vapour phases. The present chapter give a brief review of various methods used for crystal growth.

1. Crystal growth from solid state :

This method is rarely used and good quality crystals of large size cannot usually be obtained, except for certain metals where strain annealing is effective and also in certain cases where a crystal structure change occurs between the melting point and room temperature. The method of obtaining a crystal out of a polycrystalline ingot by strain annealing at high temperatures where stored energy of deformation serves as the driving force of recrystallization, is known as grain growth process.

2. Crystal growth from vapour phase :

This method is useful if the size of the crystal is not so important. But one can grow and obtain crystals with good perfection. This growth method bears its own theoretical importance and is useful to produce moderate 4 size bulk crystals. The technique has been reviewed thoroughly by Hollnad, Kaldis, Schafer, Nitsche and Wickender et al. [2-6]. This method is further divided into three categories.

(a) Sublimation:

At a suitable high temperature, sublimation of the source material takes place. The sublimated material condenses into a crystalline solid maintaining proper control over temperature and pressure conditions.

(b) Vapour Transport:

The transport of the source material takes place as a volatile species by a suitable carrier gas to the crystallization region.

(c) Gas phase reaction:

The growth of the crystals takes place as a product from the vapour phase, as a direct result of chemical reaction between the reactant vapour species. The method of crystal growth from vapour phase is rarely used to grow large crystals due to the problem of multinucleation. There are some exceptions such as CdS, ZnSe, Gap, GaAs and Cd_4GeS_6.

3. Crystal growth from aqueous solution:

This is the simplest and oldest method of growing crystals in which the material to be crystallized is dissolved in water or a suitable solvent to the desired degree of super saturation. The solution is then slowly cooled or evaporated. Using a seed crystal and precise control over temperature, humidity and rate of evaporation, excellent quality large crystals can be grown. Well-known examples are ferroelectric and piezoelectric materials such as ADP, KDP, DGA and TGS. The limitationof this method for its application to other materials are the requirements of high solubility and chemical stability of solution.

4. Gel method :

The crystal growth from gel was first reported in 1913 by leisegang, Bradford and Holmes. Substances having low solubility in water can be grown by gel method in which the constituent ions of the material slowly migrate through an inorganic or organic gel, react and from the compound. Hence the crystals grown by gel method are free from strain which is often present in the crystals prepared from melt or from vapour. During this growth, the crystal is nucleated due to the concentration of the compound which exceeds its solubility limit. This method isonly used for research because of the obvious limitations of size. The crystals liked TGS, DGS, $KClO_4$ and many others have been grown successfully by this method. The methodhas been discussed in detail by Henisch. [7]

5. Hydrothermal growth:

Crystals of many metals, their oxides and other compund which are very less soluble or insoluble in water or which may be soluble in water only at high temperatures and high pressure are grown by this method. The requirement of high pressure is a practical difficulty in this method. The size and quality of the crystals obtained by this method are poor. The industrial production of commercial piezoelectric quartz crystals is an exception. Themethod has been discussed in detail by Ballman et al [8] and James et al [9].

6. High temperature solution growth :

The method is used for the solvents having high melting point, may be above 600^0C. Though this method basically involves practical difficulties of proper choice of solvent, chemical and phase stability of the solute and solvent, high melting point, obtaining high temperatures, contamination etc., and many important materials are being grown by this method. Examples are YIG, lithium ferrite, gadolinium aluminates, barium titanate, $Ba_2MgGe_2O_7$, ruby emerald etc. This method is applicable to almost any material for which a suitable solvent can be found and yields a perfection of crystals quite higher than that obtained by any other method. Also the crystals obtained by this method have usually hight concentration of impurities than that obtained by other methods. The optimum growth rate in this method is quite small. The principles and techniques involved in this method have been discussed by Elwell et al [10].

CRYSTAL GROWTH FROM MELT:

To grow large single crystals of metals, alloys and semiconductors the most widely used method is growth from melt. Crystal growth from melt carries maximum theoretical importance also since it is directly the process of phase change from liquid to solid involving systematic aggregation of atoms or molecules into crystalline order from their random distribution in liquid state of the same substance. The basic principles of the crystal growth from melt are based on cooling of a liquid to solidification in a controlled manner. The process of solidification should be so controlled as to promote extension of single nucleus without producing new nuclei and with a minimum of nuclei. Instability of the growing surface can be eliminated by avoiding extensive zone of super-cooling in the melt. Heat transport in the solidification process plays a vital role in the success of growth. Basically the method involves transfer of heat through the solid-liquid interface. The heat transfer can be described by the equation

$K_sG_s-K_LG_L=LV$

where, K_s = thermal conductivity of solid

K_L = thermal conductivity of liquid

G_S = temperature gradient in solid

G_L = temperature gradient in liquid

L = latent heat of fusion per unit volume

V = growth velocity

If we required $G_L > 0$, clearly $V >0$, and we must have $Gs>0$.We must extract heat from the growing crystal.The melt is allowed to solidify in a controlled manner. The parameters affecting the growth process, such as the temperature gradient, the growth velocity and the composition of molten charge are crucial. In the case of some alloys, if a gradient in composition is established in the liquid during growth, there results non-uniform distribution of constituents in the alloy crystal and also the constitutional super-cooling. The composition of frozen material in such a case is always different from that of liquid or the frozen charge. Tiller et [11] and Delves[12] have shown that the constitutional super-cooling can be reduced to minimum

- → by having a steep temperature gradient
- → by having slow growth rate
- → by stirring the melt to minimize solute concentration gradient

Solute segregation occurs at the solid-liquid interface due to unequal equilibrium solute concentration in the liquid and solid states of the solvent. The segregation characterized by a segregation coefficient k, which is the ratio of equilibrium solute concentration in solid to that in liquid. In most alloy systems, $k<1$. For such cases, during crystallization, the solute concentration in the liquid near the interface will increase. The solute rejected at the interface can diffuse into the bulk of the liquid and distribute itself uniformly for sufficiently slow growth rates. In practice, however, this condition is not achieved and a concentration gradient may establish in the liquid. The solute segregation may cause

1) Crystal with non-uniform solute distribution along length of crystal

2) Constitutional super-cooling. Delves [12] has defined a parameter "S" known as constitutional super-cooling parameter which is given by

$$S = mG_{LS}/G_L$$

where,

G_{LS} = solute concentration gradient in liquid= $-V (C_L-C_S)/D$

V= growth speed

D= diffusivity of solute in liquid

C_L= concentration in liquid

C_S= required concentration in solid

m= slope of the liquids line at the given composition of alloy, in the phase diagram

G_L= temperature gradient in liquid

It has been shown that if $S > 1$, constitutional super-cooling will occur. Using slow growth rate, good stirring of the melt to minimize $G_{LS}$and using steep temperature gradient, chance of constitutional super-cooling can be greatly reduced. However, very small growth rate would require extreme care in maintaining stable thermal environment and very steep gradient would produce curved interface. The crystal growth from melt can be pictured as an atom-to-atom addition to lattice similar to the growth from vapor and the experimental evidence rule out the necessity of a screw dislocation to promote the growth of metal crystal from melt. This has been concluded from a number of observations. Firstly Das [13] has successfully grown large single crystal of silicon free from dislocation. Chalmer et al [14] have proposed a step like interface which provides permanent reentrant steps which are not propagated by dislocation and evidence of the existence of such steps has been obtained.

Study of growth of crystals from melt mainly involves:

→ Study of imperfections, their formation and distribution in the crystal

→ Study of morphology of the interface and the effect of various growth parameters on it.

→ Study of preferred orientation and the influence of various parameters responsible for this property of crystal and

→ Study of the growth features observed on the crystal grown from melt.

Many crystals have been grown from melt by various workers and many reviews have been published [15-20].

There are three basic techniques for crystal growth from melt:

1. Bridgmann method
2. Czochralski method
3. Zone melting method

1. BRIDGMAN METHOD:

This method was first developed by Bridgman [21] in 1925 to grow single crystals. The Bridgman technique (also known as Bridgman-Stockbarger method) is one of the oldest techniques used for growing crystals. Similar to Czochralski technique, the Bridgman technique employs also a crystal growth from melt. In Bridgman technique the crucible containing the molten material is translated along the axis of a temperature gradient in a furnace, whereas in Stockbarger technique, which is just a modification to the Bridgman technique, there is a high-temperature zone, an adiabatic loss zone and a low-temperature zone. These two methods are very often not specifically differed in the terminology. The crucible is then translated slowly into the cooler section of the furnace. The temperature at the bottom of the crucible falls below the solidification temperature and the crystal growth is initiated by the seed at the melt-seed interface.

After the whole crucible is translated through the cold zone the entire melt converts to a ingot of solid single crystalline material.

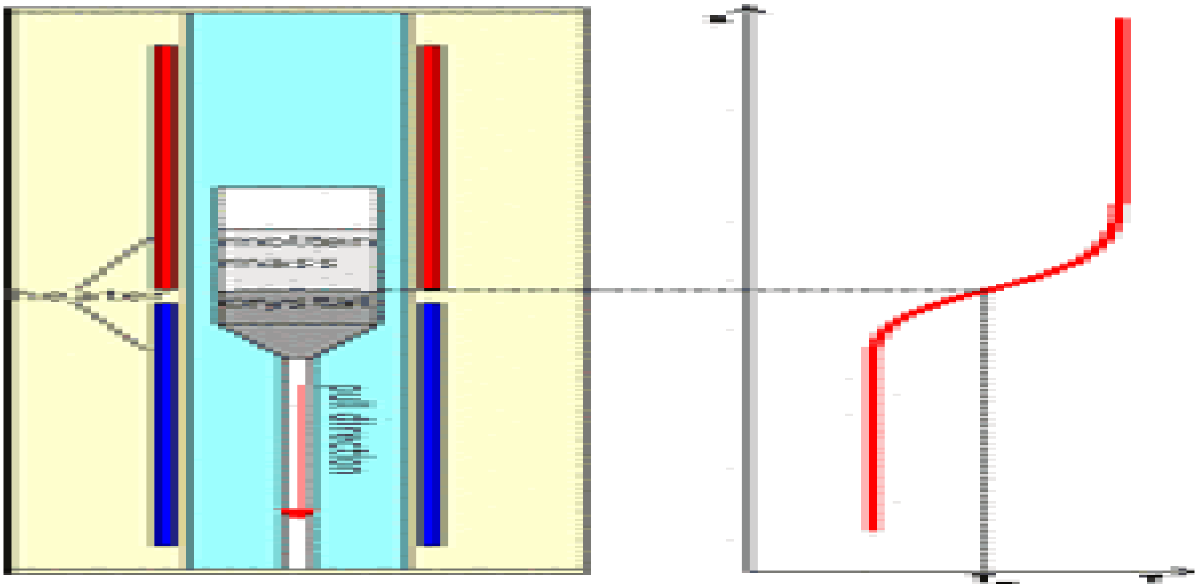

Fig 1 Furnace and temperature profile of Bridgman technique

The Bridgman technique can be implemented in either a vertical (vertical Bridgman technique) or a horizontal system configuration (horizontal Bridgman technique). The concept of these two configurations is similar. The vertical Bridgman technique enables the growth of crystals in circular shape, unlike the D-shaped ingots grown by horizontal Bridgman technique. However, the crystals grown horizontally exhibit high crystalline quality (e.g. low dislocation density) since the crystal experiences lower stress due to the free surface on the top of the melt and is free to expand during the entire growth process.

Instead of moving the crucible, the furnace can be translated from the seed end while the crucible is kept stationary. In this manner a directional solidification can be achieved, too. A further modification is the so called gradient freezing technique, with which neither the crucible nor the furnace needs to be translated. Instead, a translation of the temperature gradient is implemented by using a multiple-zone furnace wherein the power to each zone is programmed and controlled by individual controllers. This system can maintain the same temperature gradient at the liquid-solid (i.e. melt-crystal) interface, which changes in turn its location with time during the growth. Analogous to the Bridgman technique, the gradient freezing technique can also be realized in vertical and horizontal configurations.

The limitation of Bridgman method is that, it can be used only for low melting point element, which is overcome by the horizontal moving furnace technique given by Chalmers [22]this method is applied for three types of material:

1 Metals [23-24]

2 Semiconductor [25-26]

3 Alkali and Alkaline Earth halides [27-28]

Kumagawa et al [29] have grown ternary mixed crystal on InSb and GaSb seed crystals successfully, using the Bridgman method with high-speed rotation of about 80 to 120 rpm. The growth of $(Sb_XBi_{1-X})_{2Te3}$ single crystals with programmable temperature control by vertical Bridgman method has been reported by Fang-Lang Hsu [30]. Yokota et al [31] have grown Cadmium telluride crystals by horizontal two-zone Bridgman furnace in quartz ampoules evacuated to as low a pressure as 10^{-7}. Voda et al [32] have grown pure and doped CdF_2 single crystals using Bridgman method wherein unwanted vapour reaction was avoided by using an argon atmosphere and glassy carbon crucibles. Cabric et al [33] developed a method for crystallization of several substances at different rates in a chamber furnace. Eutectic intermetallic compound

SnSe has been grown by Siddiqui[34] by the Bridgman –Stockbarger method. One of the important semiconductors namely CdTe crystals are also usually grown by the Bridgman method[35].

2. CZOCHRALSKI METHOD:

In the year 1918, Czochralski[36] developed this method. Czochralski method, developed in 1971 by the polish scientist Jan Czochralski and later modified by several researchers, is one of the major melt-growth techniques. It is widely used for growing large-size single crystals for a wide range of commercial and technological applications. One of the main advantages of Czochralski method is the relatively high growth rate.

The material to be grown is first melted by induction or resistance heating under a controlled atmosphere in a non-reacting crucible. The melt is kept for a certain time at a temperature above the melting point and the temperature is then reduced to a value slightly above the freezing point.

The freezing point is judged by cooling the melt until crystals start to appear on the surface. After a further lowering of the temperature a seed (cut in the appropriate orientation) is inserted into the melt. By pulling and rotating the seed simultaneously a crystallization center forms. The diameter of the pulled crystal is controlled by manipulating the temperature of the melt and the pulling rate. Suitable engineering of both axial and radial temperature gradients is needed to grow single crystals of desired dimensions reliably.

Crystals of the various materials have been grown by this method [37-40]. Practical aspects of the technique have been treated in detail by Draper[41]. The excess of heat is removed by conduction and water circulation through the seed –holder which also helps in maintaining temperature gradient. The essential factors for obtaining a good crystal are

→ Pulling rate

→ Accurate control of temperature

→ Rotation rate of seed

Bi_2Te_3 single crystals have been grown by Laudise et al [42] using this method in H_2 and in inert atmospheres. Wenzl et al [43] have grown copper crystals by Czocharaski method in a hydrogen atmosphere at a pressure of 1 bar. A modification known as liquid encapsulated Czochralski technique has also been used [44].

In this technique, the material is melted in a porcelain, platinum or quartz crucible using a furnace. A proper choice of the crucible material has to be made, taking into account its possible chemical reaction with the material and its high temperature suitability.

A seed crystal of the material is fixed to one end of a metallic rod and the rod is lowered on to the melt surface, the seed is made to contact with the surface. The rod is then pulled up away from the melt surface at a very slow rate, ~1mm/hr. The melt adheres to the seed and is also pulled up with the rod due to its surface tension. Since the rod is at or around room temperature, a small quantity of melt sticking to the seed gets solidified. This solidified material and makes the seed grow into a larger crystal. As the pulling proceeds, more and more melt is pulled up and in this ways a large crystal is obtained. It may be required especially to keep the rod cool by circulating water around the rod. In principle, the whole mass of melt can be pulled up into a large single crystal in this way.

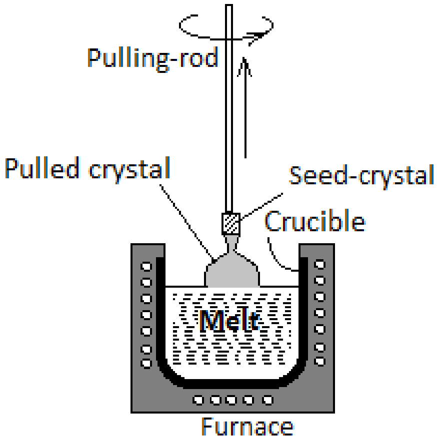

Fig 2

3. ZONE MELTING METHOD:

It is a relatively a more efficient method of growth from melt discovered by Pfann [45]. Zone refining, a precursor of floating zone technique, was first developed by W. G. Pfann in 1951 at Bell Laboratories and later modified by different people independently. Originally the floating zone technique was used for manufacturing silicon crystal, but today it can also be applied for growing single crystals of various congruently and incongruently melting oxides. During the floating zone process, a polycrystalline crystal is translated slowly through a heater and a narrow region on the crystal will be molten (floating zone). At the liquid-solid interface, the impurities diffuse from solid region into liquid region and segregate at the end of the ingot after the whole crystal passes through the heater. In order to grow a single crystal, a seed crystal having a certain orientation needs to be brought into contact with the molten region at the beginning of the process.

A variety of heating systems can be used for floating zone technique, including induction coil, resistance heater or more recently optical heating system containing high-power halogen lamps and ellipsoidal mirrors.

The main advantages of the floating zone technique are that no crucible is necessary, which results in a high purity of the grown crystal, and both congruently and incongruently melting materials can be grown by this method.

The technique has two important aspects: Impurity removal and uniform distribution of impurity, if any. In this method a small molten zone is created in a large solid ingot of the material to be crystallized and it is passed from one end of the ingot to the other end. The quality of the crystal depends on the relative zone length, growth velocity and temperature gradient. The smaller the zone length, the better is the quality of the crystal. The technique is capable of purifying a material to utmost sparse level of impurities by giving a large number of passes to the ingot in the same direction. This process is known as zone refining process. Impurities with segregation coefficient $K>1$ are collected at the end molten and frozen first, whereas the impurities with segregation coefficient $K>1$, are collected at the other end. The portion between the two ends of the ingot can be obtained purer and purer after each successive zone pass. An ingot doped with a known impurity can be made uniform in impurity distribution by the process known as zone – leveling. In this process, a molten zone is repeatedly passed through the length of the ingot in alternate directions. After several such repeated runs, effect of segregation of dopant can be virtually eliminated and the ingot can be made homogeneous. This can be efficiently done by the zone melting technique. This technique is dependent on the ratio of zone length to ingot length, speed of zone travel and the temperature gradient at the solid-liquid interface.

Parr [46] and Shah [47] have discussed in detail the theoretical and practical aspects of this method. Growth of organic compound crystals by this technique has been reviewed by Herington [48]. The use of this method to grow crystal and to refine various materials has been made by different workers, e.g. Harman et al, Richards, Hamaker, Delves, Brower et al, and Swineheart [49-54]. Balazyuk et al [55] have grown cadmium antimonite and zinc antimonite single crystals by zone melting method to study the effect of crystal growth condition on the structural perfection and thermal properties. Lunin et al [56] have studied the distribution in various layers of $AlxGa1_{-x}Sb$ growing in a temperature gradient field. Shukla et al [57] have grown $CdBr_2$ single crystals by the zone melting method. Interestingly, Serra et al [58] have successfully grown large area zinc sheet crystals by using a modified zone melting method. This is a hybrid of the zone melting and the horizontal Bridgman techniques. Zhanguo et al [59] have used the zone melting method for preparing YBaCuO superconductor successfully.

We can move a small molten zone all across whole length of the polycrystalline material, ultimately converting the whole length into a single crystal.

In the direction of travel, zone will melt while, in the opposite direction of travel, freezing occurs.

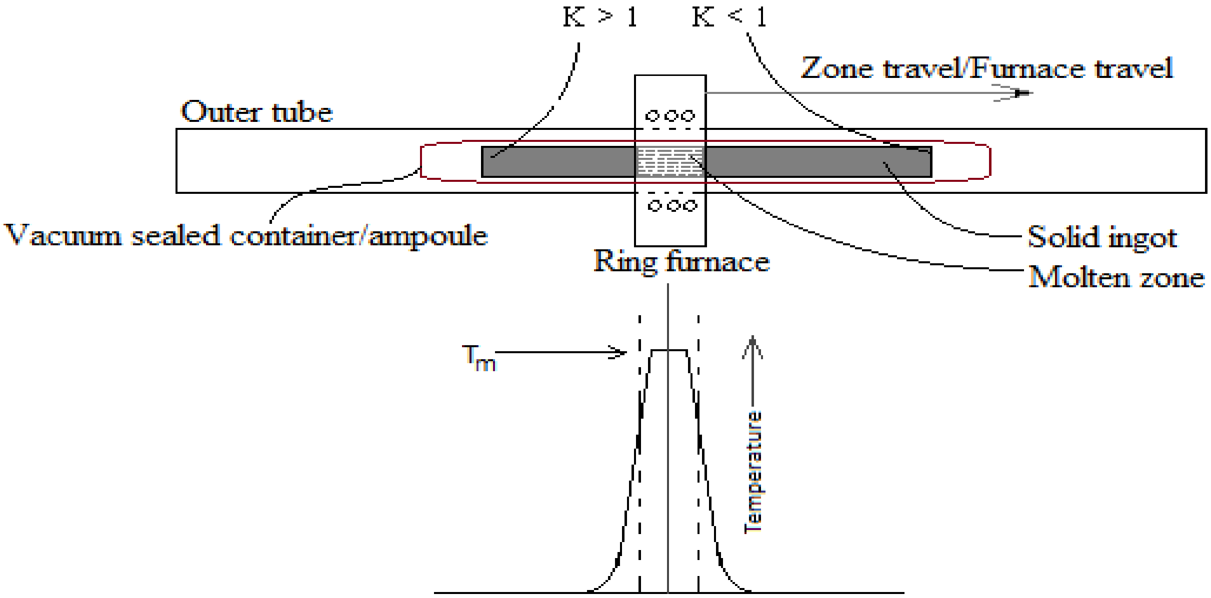

Fig 3 ZONE MELTING METHOD

SYNTHESIZING THE COMPOUND

In order to ensure a uniform charge for crystal growth, an alloy mixing unit was used and it is described in chapter 2.

The elements used, viz., antimony, bismuth and tellurium were each of 5N purity purchased from either Koch Light Laboratories, England or Nuclear Fuel Complex, Hyderabad. The stoichiometric proportions of all the components were weighed accurately up to 10 microgram using a semi microbalance and filled in a quartz ampoule of about 10 cm length and 1 cm diameter. The quartz tube of the horizontal furnace and was kept inactive for almost a day. The temperature was kept about 50ºC above the melting point of the alloy, i.e., about 630ºC. and so the quartz tube was turned out at one r. p. m by a motor attached to one of its goals. The revolution of the quartz tube gives rocking movement to the ampoule and stirs the molten charge. Normally, ten rotations followed by an idle run of one-day is found sufficient. After this, the molten charge is slowly cooled. This procedure produces fairly homogeneous alloys of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2).

CRYSTAL GROWTH

For the crystal growth of $Bi_{2-x}Sb_xTe_3$(x=0, 0.05, 0.1, 0.2) by the Bridgman technique, the ampoule with the ingot was kept in the vertical Bridgman furnace. The length of the core of the furnace is about 45 cm. The temperature profile of the furnace is shown in fig.4. The ampoule was kept steady for 24 hours in the upper hot zone of the furnace and then lowered into the cold zone at a rate of 0.35 cm/hr and through a temperature gradient of about 45ºC/cm. The crystal were obtained 3.5 cm in length and 1.2 cm in diameter. They could be cleaved easily. Microscopically the cleavage plane of the crystal was found to planar. These crystals have (111) cleavage.

The single crystals of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2) were prepared using the zone melting method also. The temperature profile of the zone furnace is shown in fig. 5. The starting ingot was synthesized as mentioned above and then to level of impurities, 8 passes in alternate directions were made and in the end the final passport was used to obtain self-nucleated single crystals. The temperature gradient across the two solid-liquid interfaces was about a 50ºC / cm giving a zone length of approximately 8 to 10 mm with a maximum temperature of 630ºC. The growth velocity was 0.35 cm/hr. To obtain good crystals it is necessary to devote sufficient time to the first molten zone before taking off the zone travel to achieve stable conditions.

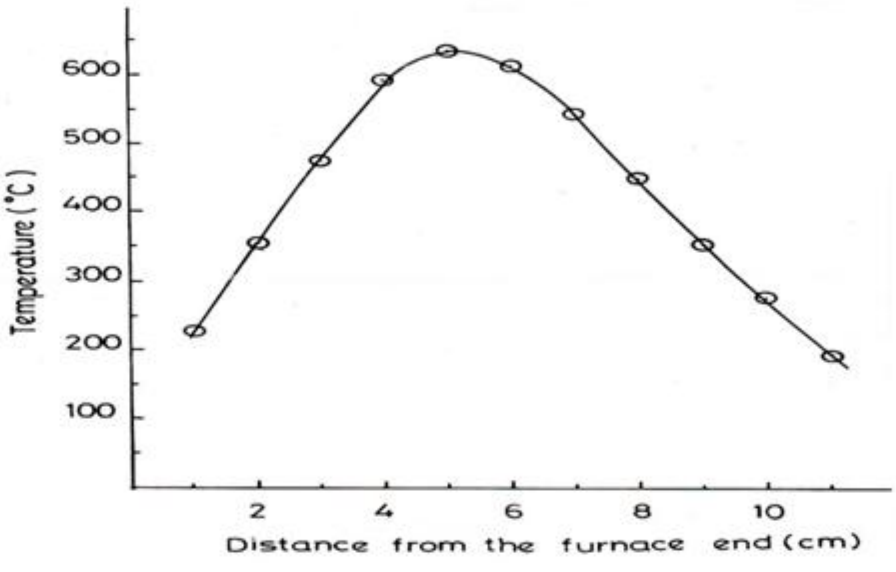

Fig. 4 TEMPERATURE PROFILE FOR BRIDGMAN FURNACE

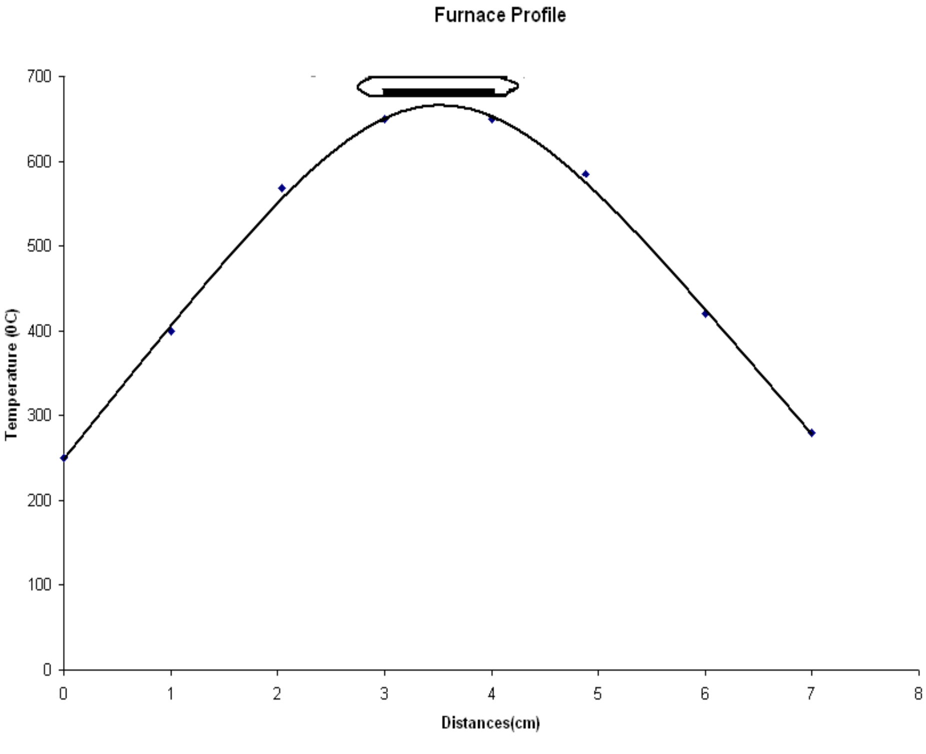

Fig.5 TEMPERATURE PROFILE FOR ZONE MELTING FURNACE

Surface study of crystals (surface topography)

The term crystal morphology implies the study of crystal forms. Mainly morphology is concerned with minerals but in modern scenario crystal morphology encompasses the external features as well as the internal structure of crystal like zone and pyramids of growth, cleavage cracks, inductive surface etc. Surface morphology is not only an indicator of internal crystal perfection, but it also provides a link between this perfection, growth rate and growth conditions.

Hence the present study of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2) for observation of crystal surfaces grown by Zone-melting and Bridgman technique, electron microscopy has been used.

Crystallographic features onthe as-grown crystal surfaces of metals, semiconductors and their alloys have been observed by various workers [60-63]. These feature specified such condition of crystal growth Mourizone et al. [64] observed features in the form of striations in InSb crystals. These striations were recognized as impurity not to the orientation and growth rate, but are rather dependent on the convection currents in melt. Striation parallel to the growth axis have also been reported by Teghtsoonian and Chalmers [65] who associated the striations to the cellular structure of the solid-liquid interface. In the case of Bi-Sb alloy crystals, Bhatt et al. [66, 67] observed striations on the free surface of the as- grown crystals as well as triangular and hexagonal crystallographic features on the cleavage plane. They have reported that these features are dependent on the growth rate and alloy composition and have shown that the striations are a result of dendritic growth arising due to growth anisotropy which varies with alloy composition.

In the case of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2) crystals by Bridgman method no growth features have so far been reported. However, the present author has observed some interesting features on the as-grown single crystals and these are represented as;

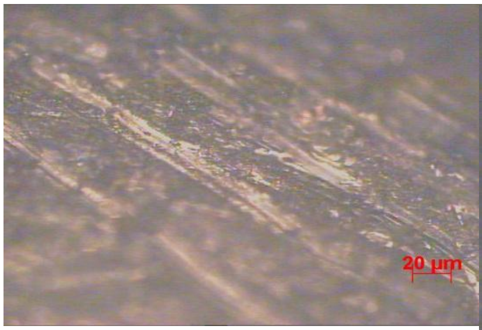

Fig.6

Fig.7

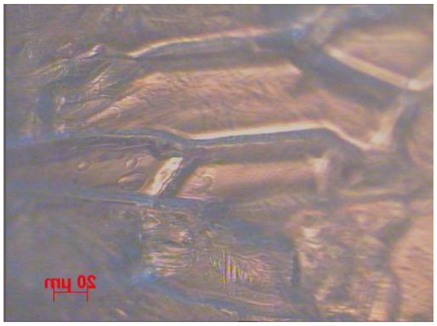

Fig.8

Fig.9

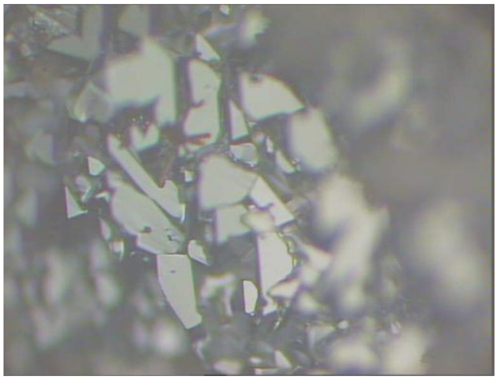

Fig.10

Fig.6 shows a parallel striation in the case of $Bi_{1.95}Sb_{0.05}Te_3$ crystal. Fig.7 shows similar striations but a superimposed growth hillock which is of equilateral triangular shape. On these two photographs above need compared with Fig.8 which shows a cellular growth step. The angles in the geometry of this structures all were measured to be 120° to the 3-fold symmetry patient to the crystal which belongs to the rhombohedral structure type. The direction of the edges and the planes involved in all these features therefore correspond to (111), respectively. The phenomenon associated with these growth features should closely parallel the one observed and explained in the case of Bi_2Te_3 alloy nanocrystal[68]. On Fig.6 we also classify that it is possible that some crystallographic plane like (111) may be responsible for these features [69]. For the same growth velocity, dendritic features were also observed on top free surface of the crystals, these are shown in Fig.9. The crystal flakes due to vapour condensation of the surface is shown in Fig.10. These features indicate each Bi_2Te_3 flake probably is a single crystal with (111) flat surface. The phenomenon associated with these growth features should closely parallel the one observed and explained in the case of ZnO single crystal [70].

ENERGY DISPERSIVE ANALYSIS OF X-RAYS

In the case of 3rd–5thelements and compound containing group 6th elements the difference in vapour pressure and reactivity of the volatile components result in change of the stoichiometry of the melt. This change in turn corresponds to the changes in other properties of the material (crystal).The present day understanding of the properties of the thermoelectric material is dependent complete chemical analysis which encompasses various aspects including identification of various elements present, quantitative chemical composition, chemical state of the elements and distribution of vapour pressure in order to effect melt and hence crystal stoichiometry, is a desirable feature of any technique. The present study concentrates on the detection and quantitative and distributional analysis of the components present in the Bridgman grown crystals,viz,$Bi_xSb_{2-x}Te_3$ (x=0, 0.05, 0.1, 0.2).The compositional analysis has been done by the Energy Dispersive Analysis of X-rays (EDAX). It is an attachment to the advanced electron microscope for chemical analysis. The principle underlying EDAX is as follows: When the beam of electrons strikes a specimen a fraction of the incident electrons excites the atoms of the specimen which then exits X-rays strictly related to the atomic number of the elements excite and there after their deflection forms the basis of elemental analysis. EDAX gives information about chemical composition or phases in which they exist.

According to Horak and Mzerd orderly in $Sb_2Te_{2.948}$ and Sb_2Te_3 have shown usually non-stoichiometric annealing [71,72].

Fig.11-14 shows the energy Dispersive Spectra (EDS) of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2) single crystal. Table 2 shows the atomic % of Bi, Sb, Te, in $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2).

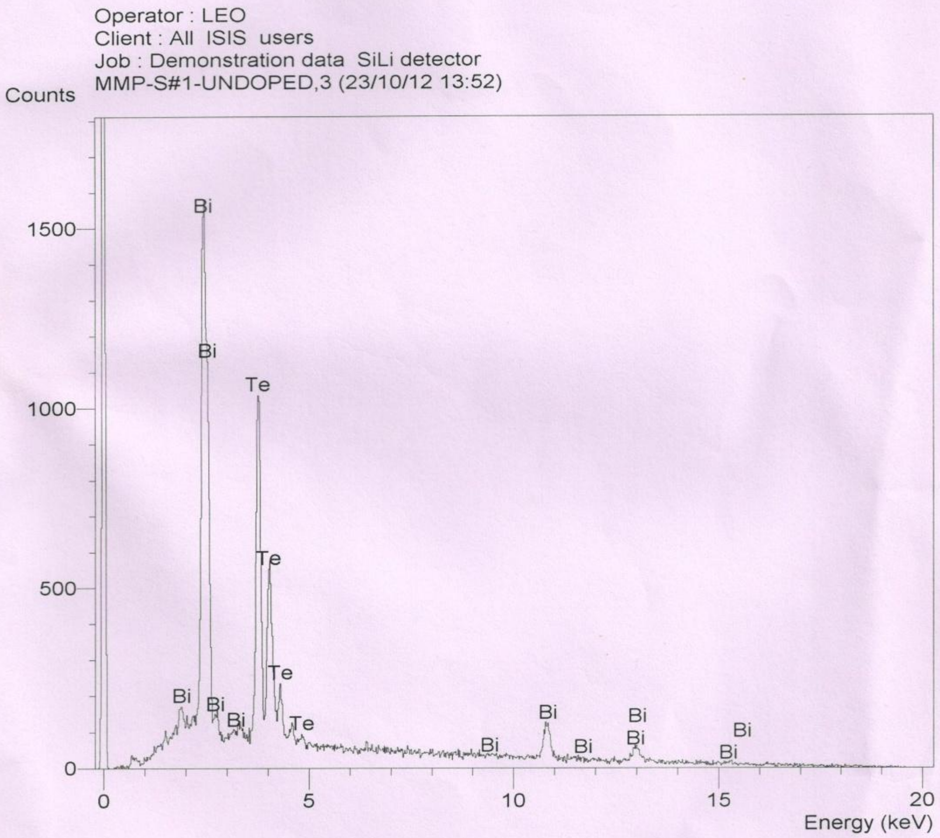

Fig.11 EDAX SPECTRA OF Bi_2Te_3 SINGLE CRYSTAL

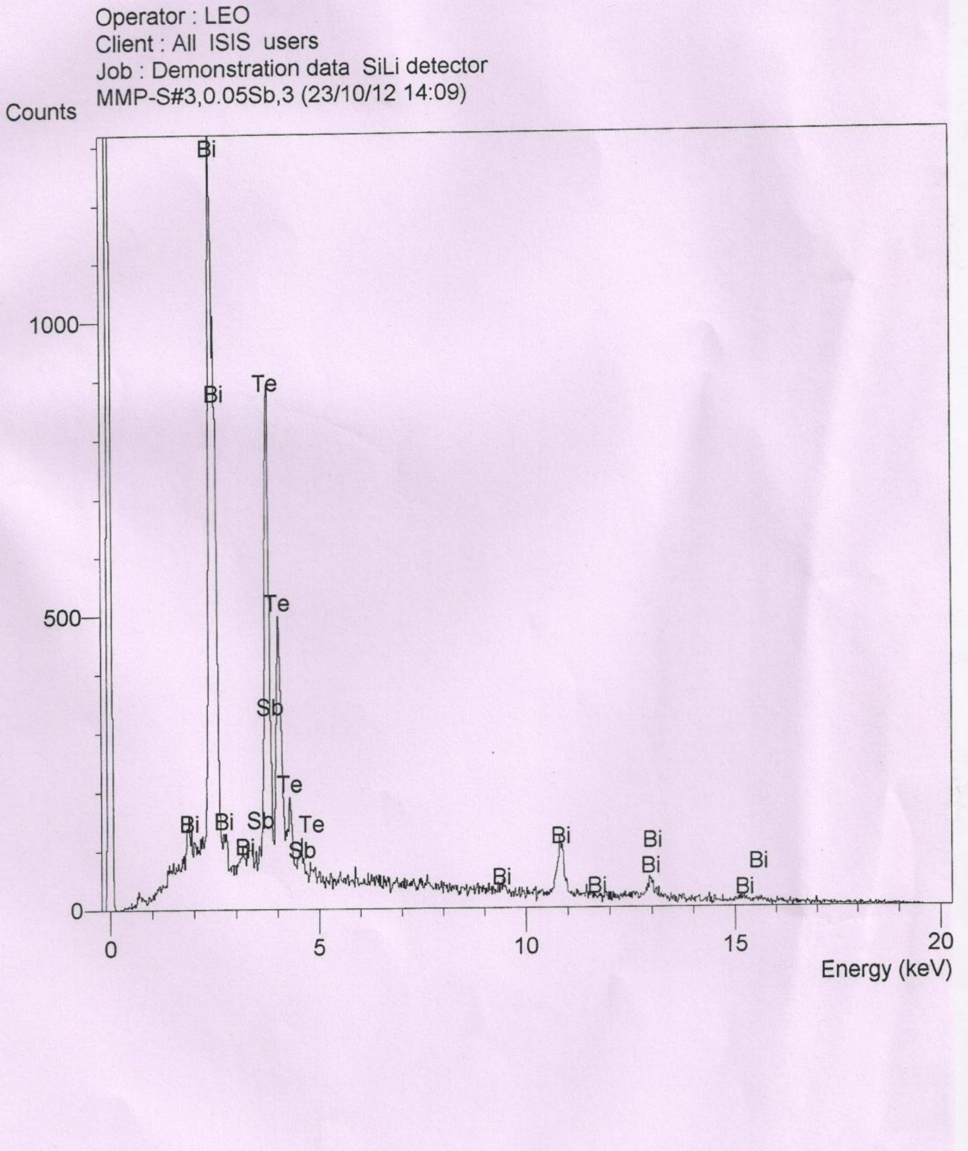

Fig.12 EDAX SPECTRA OF $Bi_{1.95}Sb_{0.05}Te_3$ SINGLE CRYSTAL

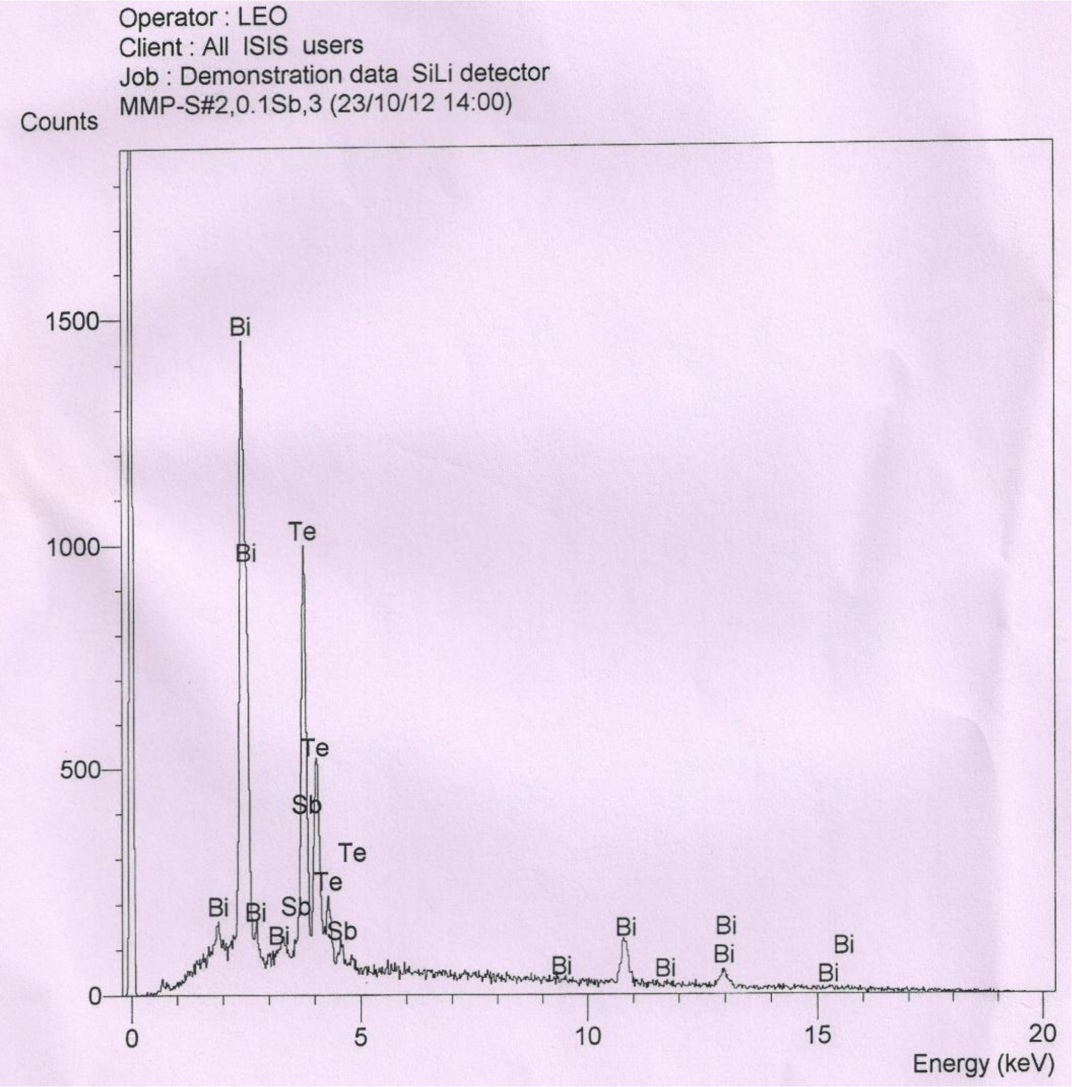

Fig.13 EDAX SPECTRA OF $Bi_{1.90}Sb_{0.1}Te_3$ SINGLE CRYSTAL

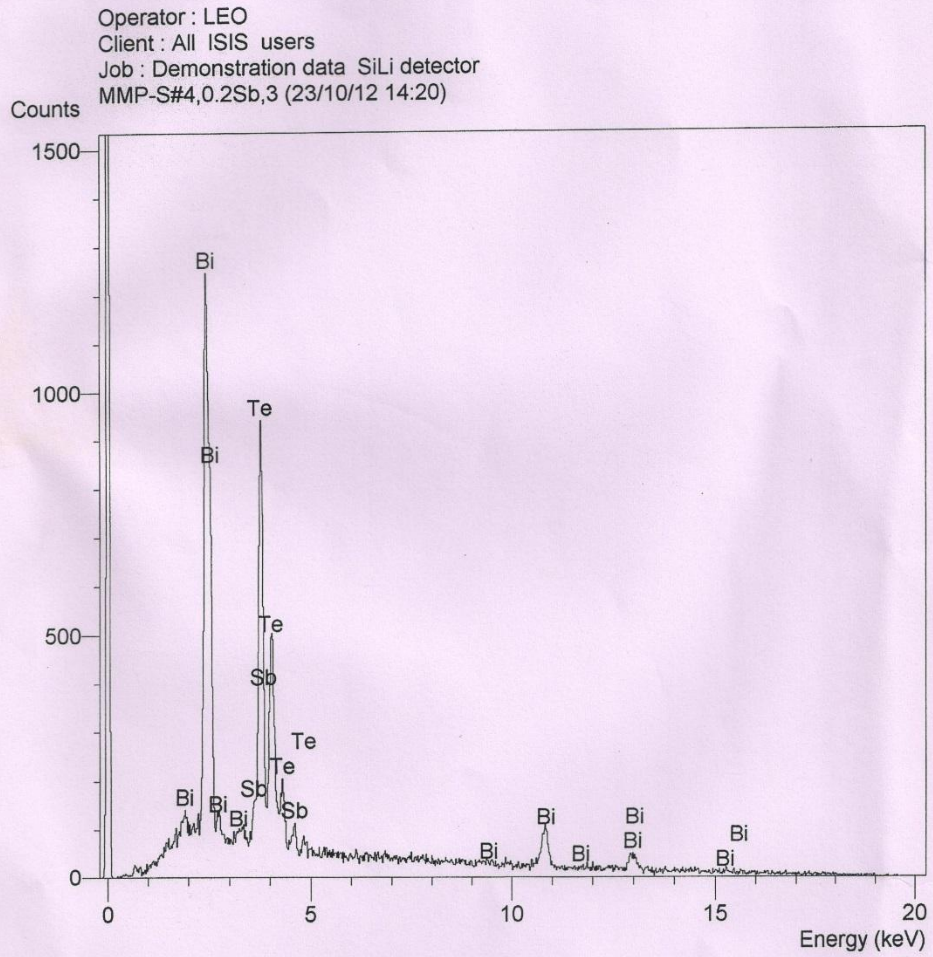

Fig.14 EDAX SPECTRA OF $Bi_{1.8}Sb_{0.2}Te_3$ SINGLE CRYSTAL

Table.2

Compositional Analysis of 3 Different Regions from $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2) single crystal

Crystal	Element Present	Atomic%
Bi_2Te_3	Bi Te	39.40 60.60
$Bi_{1.95}Sb_{0.05}Te_3$	Bi Sb Te	38.05 2.30 59.65
$Bi_{1.9}Sb_{0.1}Te_3$	Bi Sb Te	37.87 2.76 59.38
$Bi_{1.8}Sb_{0.2}Te_3$	Bi Sb Te	36.10 4.80 59.11

X-Ray diffraction analysis:

X-ray diffraction techniques are useful tools for structural investigations of bulk and thin films. The powder X-ray diffraction technique in particular, has been used for structural analysis.

Amin et at al.[73] have used metallographic techniques in conjunction with X-ray powder diffractions pattern to assess the homogeneity of the pseudo-binary and ternary alloys (75% Sb_2Te_3-25%Bi_2Te_3) p-type and (90% Bi_2Te_3-5% Sb_2Te_3-5%Sb_2Te_3) n-type alloys prepared by hot or cold or sintering pressing method to reveal any precipitations. Both of these alloys, whether grown by the Bridgman method or the travelling heater method, produce bi- or tri crystals. X-ray orientation of these crystals showed the (111) plane to be lying within 10º-15º of the freezing direction (direction of crystal ingot axis). Bi_2Te_3 – related pseudo-binary and ternary alloys have been extensively studied in single crystal from [74, 75, 76, 77]. Mzerd et al.[72] have shown that the relative intensities of various peaks obtained by x-ray diffraction of the annealed samples of Sb_2Te_3 are greater than those in the case of unannealed samples and this is due to change in stoichiometry. Francombe [78] has reported that upon heating, the c-axis of the hexagonal unit cell expands more rapidly than the a-axis. Shvangiradze et al.[79] studied the alloys $(Bi_{0.12}Sb_{0.88})_{1-y}Te_y$(y=0.57-0.615) by the methods of x-ray phase and metallographic analysis. According to the data obtained, alloys with a tellurium content exceeding 60.2 atiomic % are two-phase materials; they consist of a matrix phase (the solid solution $Bi_{0.24}Sb_{1.76}Te_3$) and tellurium, whose quantity increases together with the tellurium content in the starting charge.

In the present study, X-ray diffractrometer with copper target has been used for obtaining the powder diffraction pattern of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2). The x-ray generator was operated at 45kV and 40mA. The diffractrometer used has a radiation counter to measure the angular position and intensity of the diffracted beam. A recorder automatically plots the intensity of the diffracted beam as the counter moves on a goniometer circle which is in synchronization with the specimen over the selected range of 2θvalue.

Typical X-ray data diffraction spectra of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.9}Sb_{0.1}Te_3$, and$Bi_{1.8}Sb_{0.2}Te_3$crystal powders are shown in Fig.15-18, respectively. The pattern consists of well-defined sharp diffraction lines indicating good crystallinity of the specimen. Table 3 shows the indexing of the diffraction pattern. The identification of peaks in diffraction intensity was made using a JCPDS (File) NO.15-863 & 15-874 [International Center for Diffraction data, Pennsylvania, U.S.A.,].The compound and index assignments are indicated on the major peaks in the respective plots. The observed and the JCPDS file d values are found to be in fair agreement [81]. Table 4 shows the lattice parameters values of the c and a, evaluated from the X ray data.

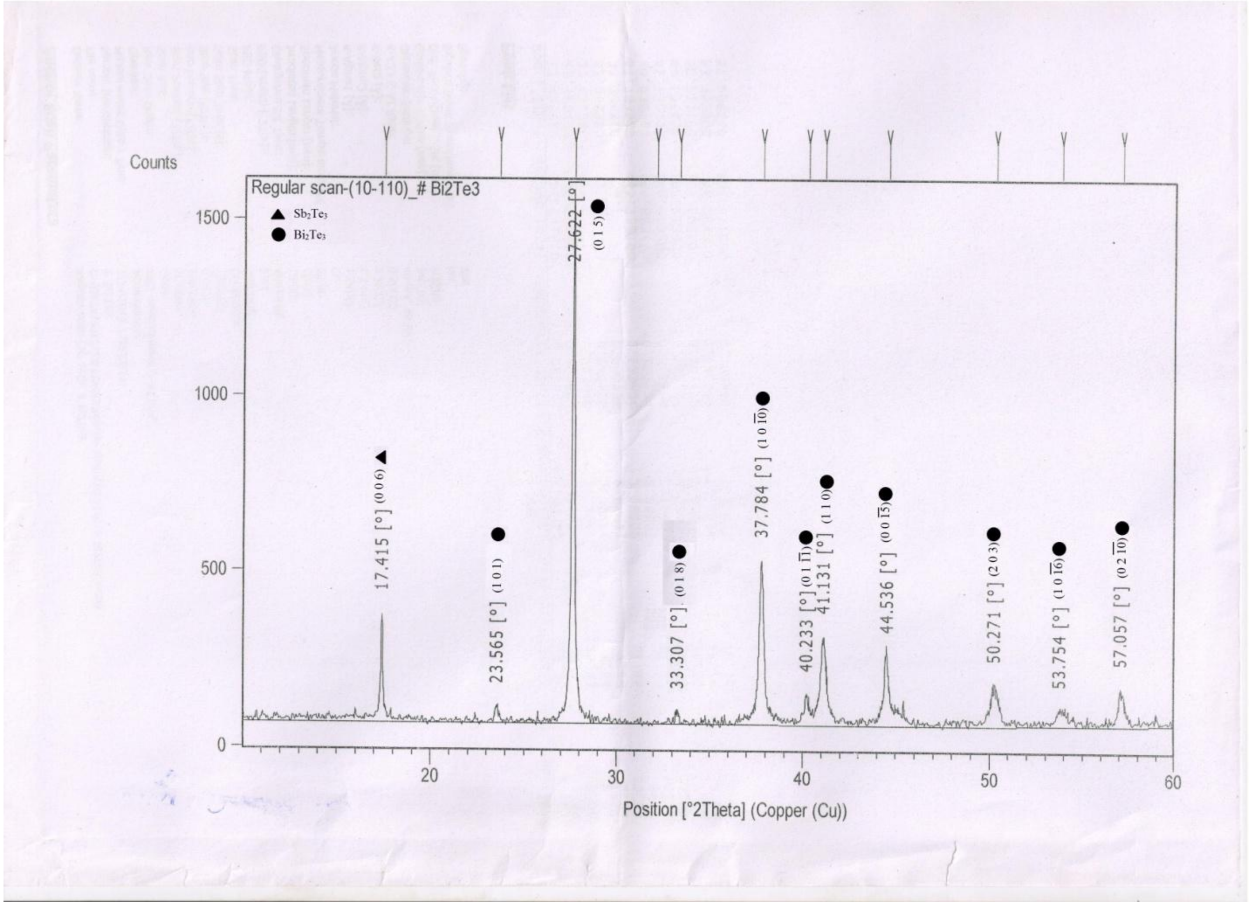

Fig.15

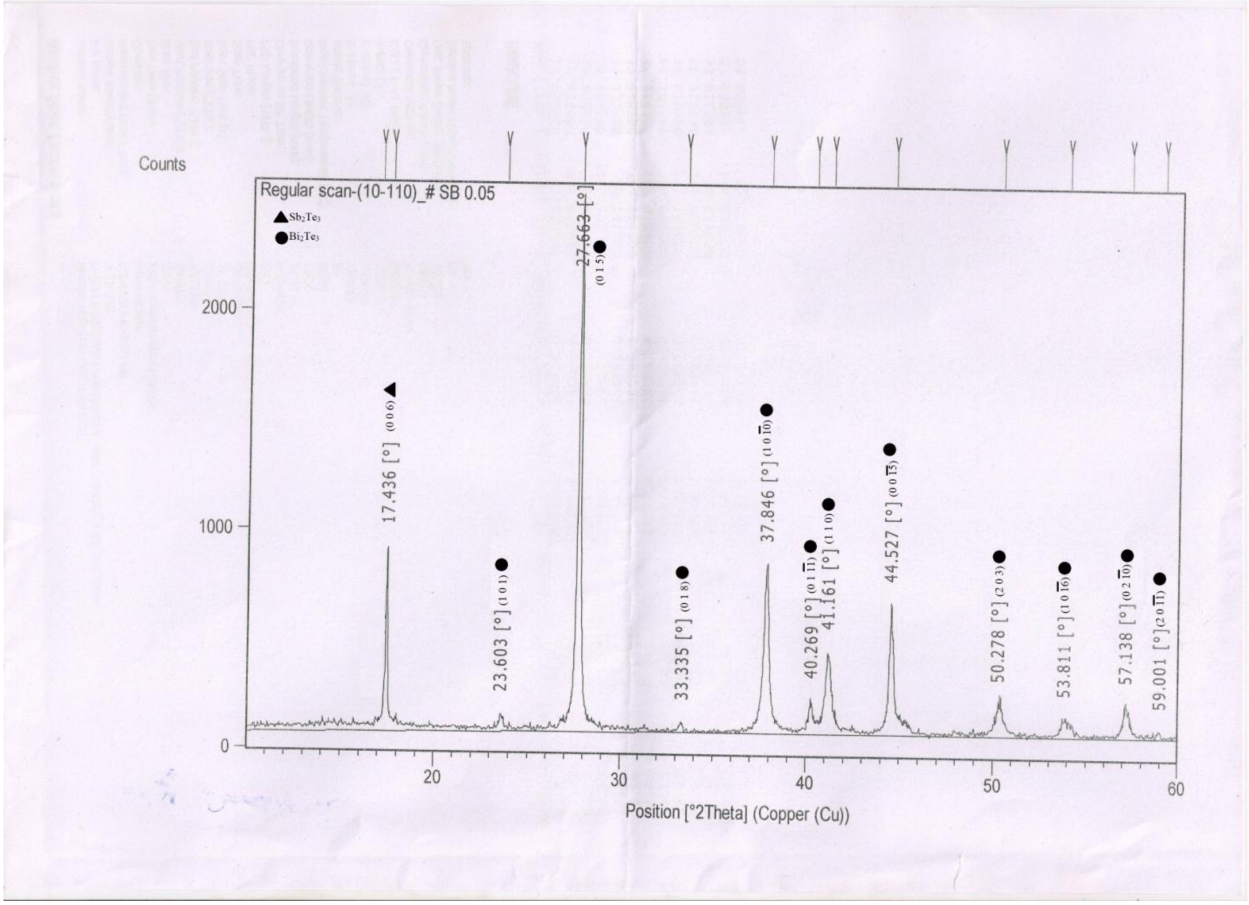
Counts
Regular scan-(10-110)_# SB 0.05
▲ Sb_2Te_3
● Bi_2Te_3
2000
1000
0
17.436 [°] (0 0 6) ▲
23.603 [°] (1 0 1) ●
27.663 [°] (0 1 5) ●
33.335 [°] (0 1 8) ●
37.846 [°] (1 0 $\overline{10}$) ●
40.269 [°] (0 1 $\overline{11}$) ●
41.161 [°] (1 1 0) ●
44.527 [°] (0 0 $\overline{15}$) ●
50.278 [°] (2 0 3) ●
53.811 [°] (1 0 $\overline{16}$) ●
57.138 [°] (0 2 $\overline{10}$) ●
59.001 [°] (2 0 $\overline{11}$) ●
20
30
40
50
60
Position [°2Theta] (Copper (Cu))

Fig.16

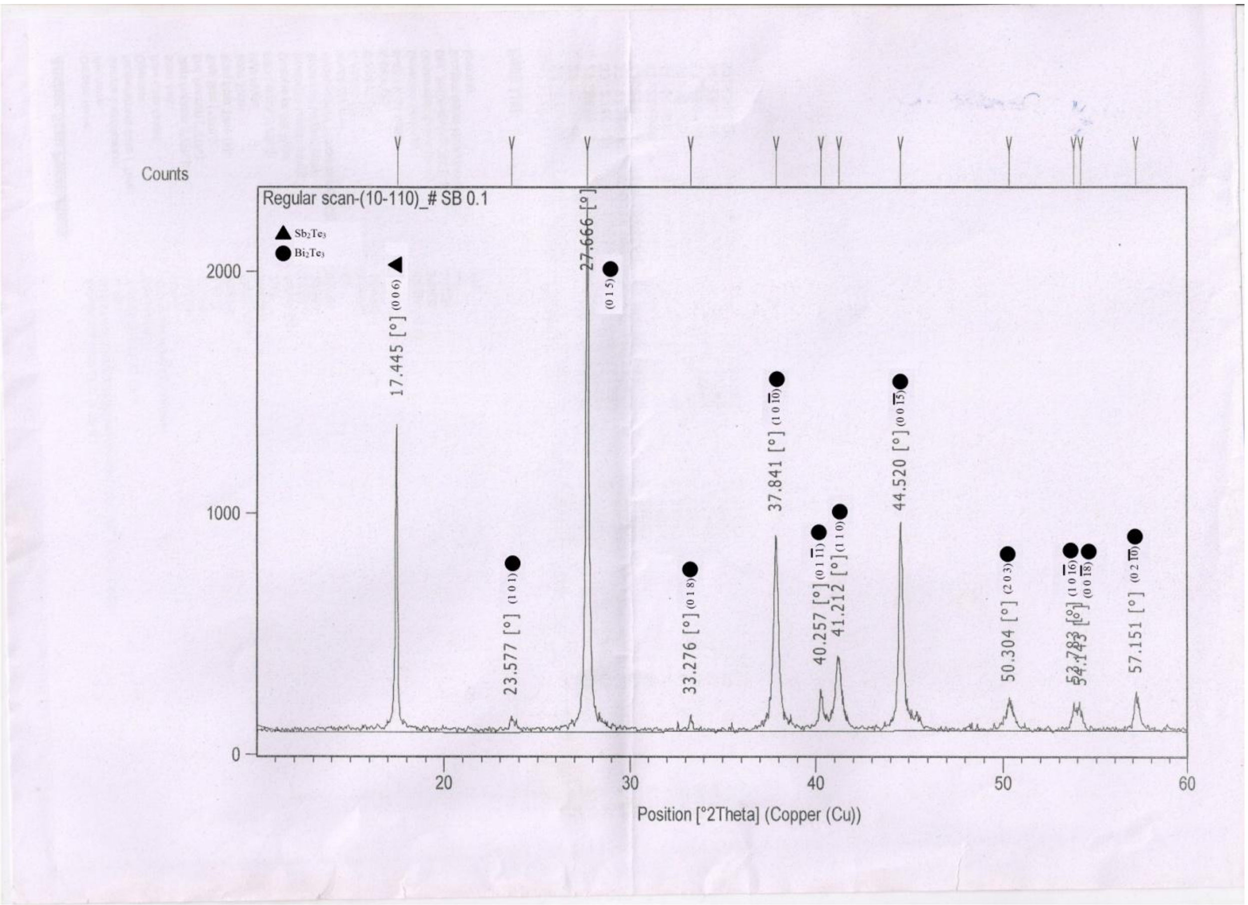
Counts
Regular scan-(10-110)_# SB 0.1
▲ Sb2Te3
● Bi2Te3
2000
1000
0
17.445 [°] (0 0 6)
27.666 [°] (0 1 5)
23.577 [°] (1 0 1)
33.276 [°] (0 1 8)
37.841 [°] (1 0 10)
40.257 [°] (0 1 11)
41.212 [°] (1 1 0)
44.520 [°] (0 0 15)
50.304 [°] (2 0 3)
53.783 [°] (1 0 16)
54.143 [°] (0 0 18)
57.151 [°] (0 2 10)
20
30
40
50
60
Position [°2Theta] (Copper (Cu))

Fig.17

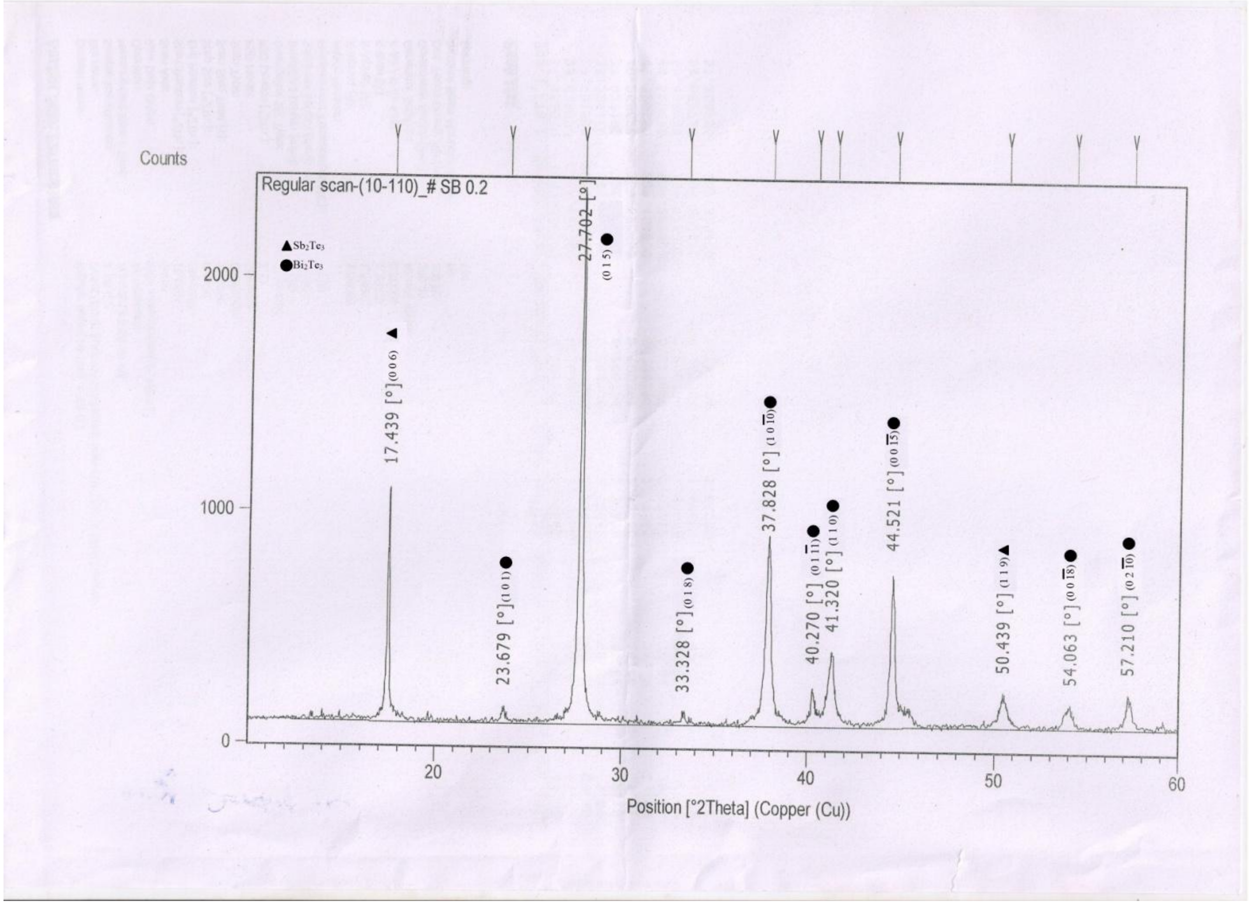

Fig.18

Table 3

Lattice parameter of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2)

Crystal	a (Å)	c (Å)
Bi_2Te_3	4.393	3.055
$Bi_{1.95}Sb_{0.05}Te_3$	4.387	3.051
$Bi_{1.90}Sb_{0.1}Te_3$	4.386	3.041
$Bi_{1.8}Sb_{0.2}Te_3$	4.309	3.062

Table.4

Diffraction data of $Bi_{2-x}Sb_xTe_3$ (x=0, 0.05, 0.1, 0.2) single crystal

Bi_2Te_3		$Bi_{1.95}Sb_{0.05}Te_3$		$Bi_{1.90}Sb_{0.1}Te_3$		$Bi_{1.8}Sb_{0.2}Te_3$	
d A°	(h k l)	d A°	(h k l)	d A°	(h k l)	d A°	(h k l)
5.09232	(0 0 6)	5.08627	(0 0 6)	5.08368	(0 0 6)	5.08541	(0 0 6)
3.77539	(1 0 1)	3.76952	(1 0 1)	3.77354	(1 0 1)	3.75752	(1 0 1)
3.22947	(0 1 5)	3.22475	(0 1 5)	3.22444	(0 1 5)	3.22036	(0 1 5)
2.69011	(0 1 8)	2.68788	(0 1 8)	2.69253	(0 1 8)	2.68842	(0 1 8)
2.38102	(1 0 $\overline{10}$)	2.37727	(1 0 $\overline{10}$)	2.37755	(1 0 $\overline{10}$)	2.37836	(1 0 $\overline{10}$)
2.24157	(0 1 $\overline{11}$)	2.23964	(0 1 $\overline{11}$)	2.24027	(0 1 $\overline{11}$)	2.23960	(0 1 $\overline{11}$)
2.19468	(1 1 0)	2.19312	(1 1 0)	2.19054	(1 1 0)	2.18505	(1 1 0)
2.03444	(0 0 $\overline{15}$)	2.03317	(0 0 $\overline{15}$)	2.03517	(0 0 $\overline{15}$)	2.03512	(0 0 $\overline{15}$)
1.81499	(2 0 3)	1.81476	(2 0 3)	1.81387	(2 0 3)	1.80935	(1 1 9)
1.70534	(1 0 $\overline{16}$)	1.70364	(1 0 $\overline{16}$)	1.70448	(1 0 $\overline{16}$)	1.69631	(1 0 $\overline{18}$)
1.61421	(0 2 $\overline{10}$)	1.61211	(0 2 $\overline{10}$)	1.69400	(1 0 $\overline{18}$)	1.61026	(0 2 $\overline{10}$)
		1.56558	(2 0 $\overline{11}$)	1.61177	(0 2 $\overline{10}$)		

These experimental values are in good agreement with the literature ones [80-81]. The pattern show no new peaks introduced by Sb indicating have substitutional position in the Bi_2Te_3 lattice and Sb_2Te_3 lattice. No reflection corresponding to the free elements, if any, were detected in the diffraction pattern.

FTIR ANALYSIS

The term "infra-red" covers the range of the electromagnetic spectrum between 0.78 and 1000 millimeter. In the context of infrared spectrum analysis, wavelength is measured in "wave numbers", which cause the units cm-^{1}.

Wave number = 1 / wavelength in centimeters

It is useful to divide the infrared region into three sections; near, mid and far infrared;

Region	**Wavelength range** (mm)	**Wave number range** (cm^{-1})
Near	0.78 - 2.5	12800 – 4000
Middle	2.5 – 50	4000 – 200
Far	50 -1000	200 – 10

The most useful IR. region lies between 4000 - 670cm^{-1}. IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states.

For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the atom. The alternating electrical field of the radiation (remembers that electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the atom. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be engaged, having a change in the amplitude of molecular vibration.

The I.R. Spectrophotometer (FTIR, Japan,Jasco, 4100)**[8]** was used for measurement of optical absorption of the samples. In the case of crystals, fine crystalline powder was thoroughly mixed with spectroscopic grade dry KBr powder at about less than 5% concentration and the mixture was formed into a palette of about 1 cm diameter, using vacuum palletizer. The optical absorption was measured in the wave number range 400 cm^{-1} to 4000 cm^{-1} and the absorption spectrum was recorded. By analyzing the spectrum, absorption coefficient was calculated as function of photon energy. Since in the pelettized samples, the material thickness is undetermined, an arbitrary coefficient. However, the relative variations only are significant for the purpose of evaluating optical band gap. The dependence of the absorption coefficient α on photon energy E near the absorption edge is given by

$$\alpha = A\,(E-E_g)^n$$

Where A is a slowly varying function which may be regarded as a constant over narrow range considered and n is a number which depends on the nature of the transition. n is equal to 1/2 for a direct allowed transition, 3/2 for a direct forbidden transition, 2 for an indirect allowed transition and 3 for an indirect forbidden transition.

The plots of $(\alpha h\upsilon)^2$ vs hυ were used to evaluate the optical band gaps. These plots are shown in Fig. 19-22 for $Bi_{2-x}Sb_xTe_3$ (x = 0, 0.05, 0.1, 0.2). 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 $(\alpha h\upsilon)^2 = 0$, the band gap was evaluated. It is observed that there is a increase in band gap with the increase of Sb concentration in Bi_2Te_3 . While the results obtained for Bi_2Te_3 are in good agreement[82]. The valued of the band gap obtained are given in Table.5.

Table.5

Crystal	Direct gap eV
Bi_2Te_3	0.16
$Bi_{1.95}Sb_{0.05}Te_3$	0.18
$Bi_{1.9}Sb_{0.1}Te_3$	0.19
$Bi_{1.8}Sb_{0.2}Te_3$	0.22

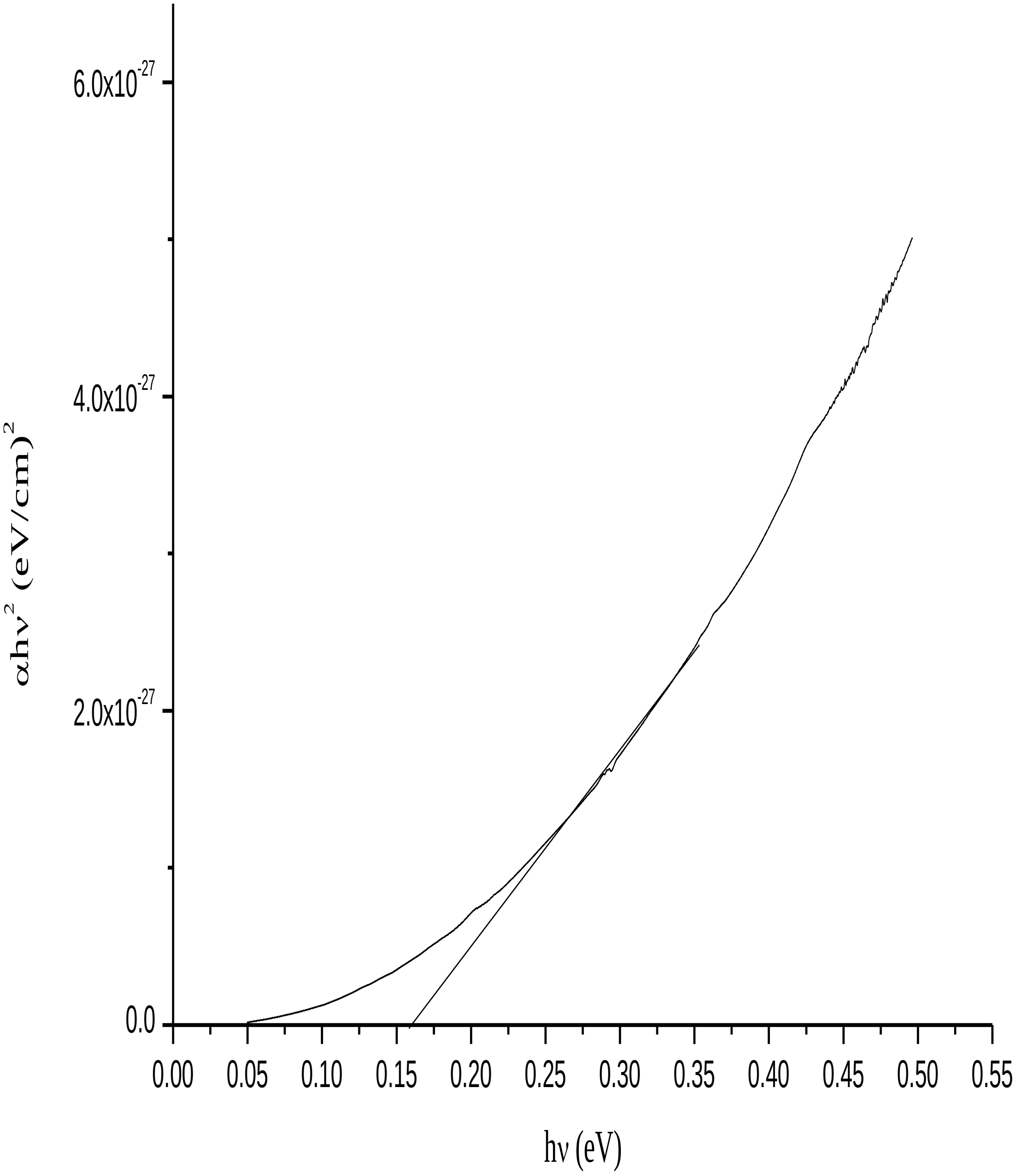

Fig.19 Band Gap of Bi_2Te_3 crystals

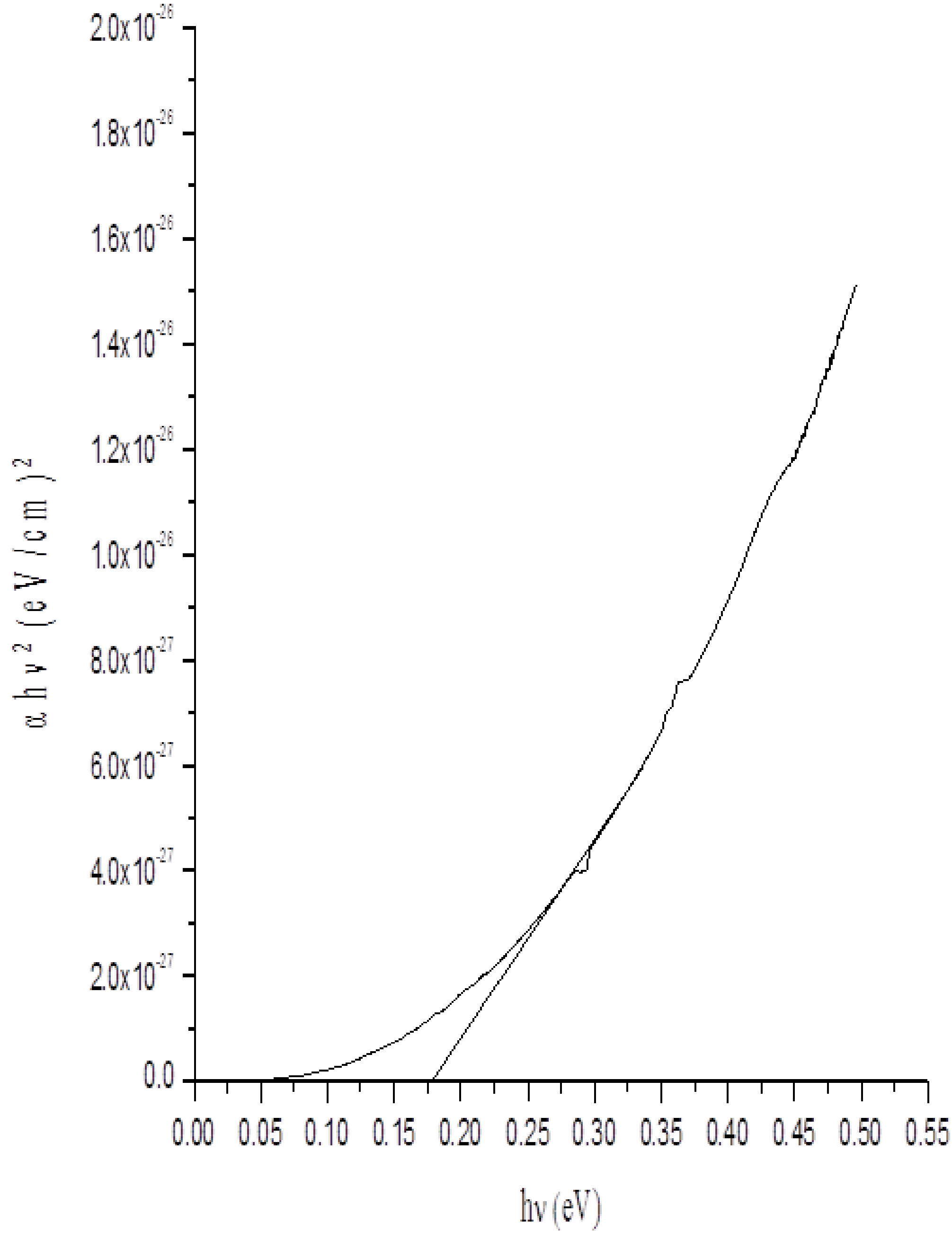

Fig.20 Band Gap of $Bi_{1.95}$ Sb $_{0.05}Te_{3.}$crystals

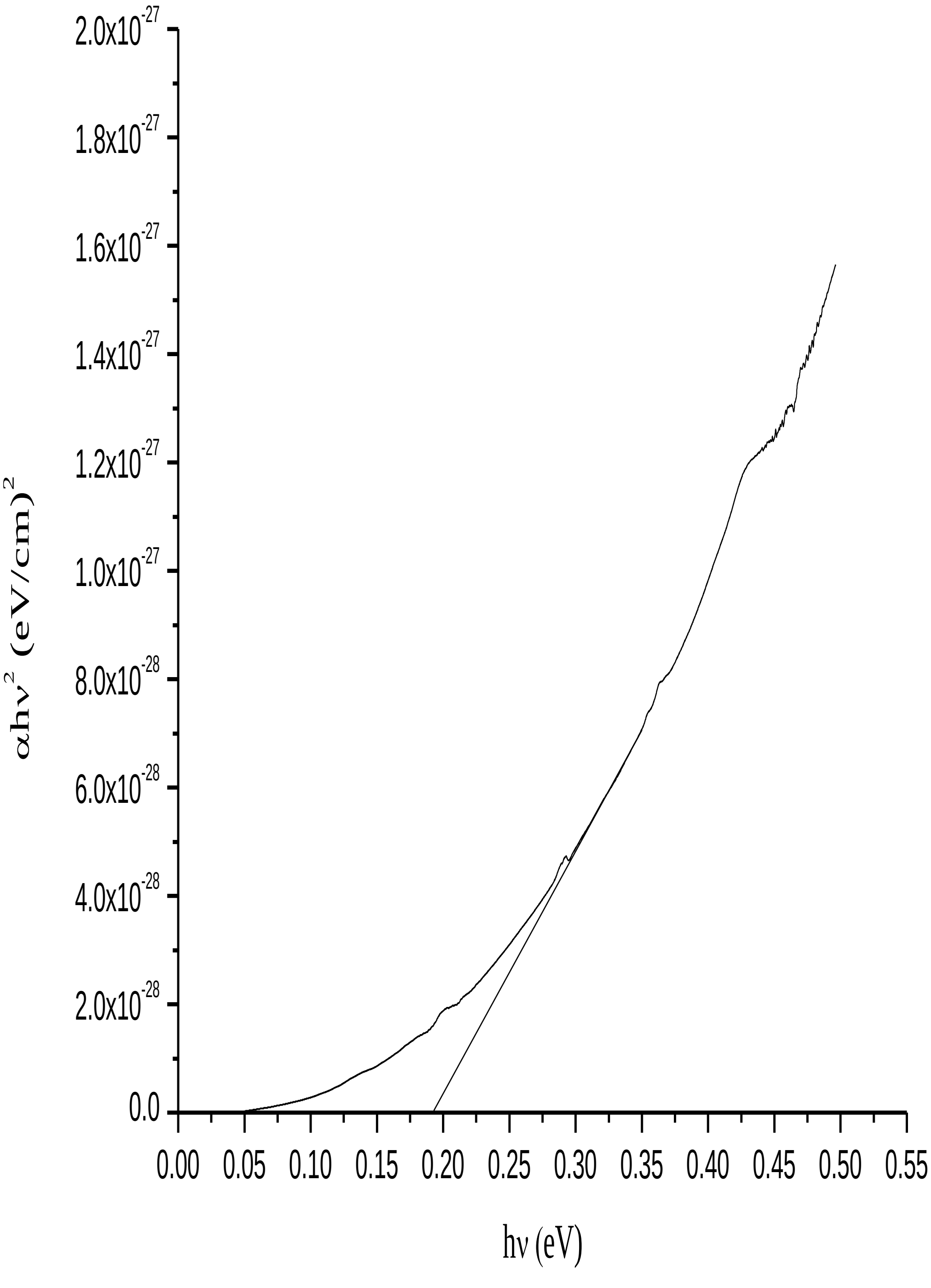

Fig.21. Band Gap of $Bi_{1.9}$ Sb $_{0.1}Te_{3.}$crystals

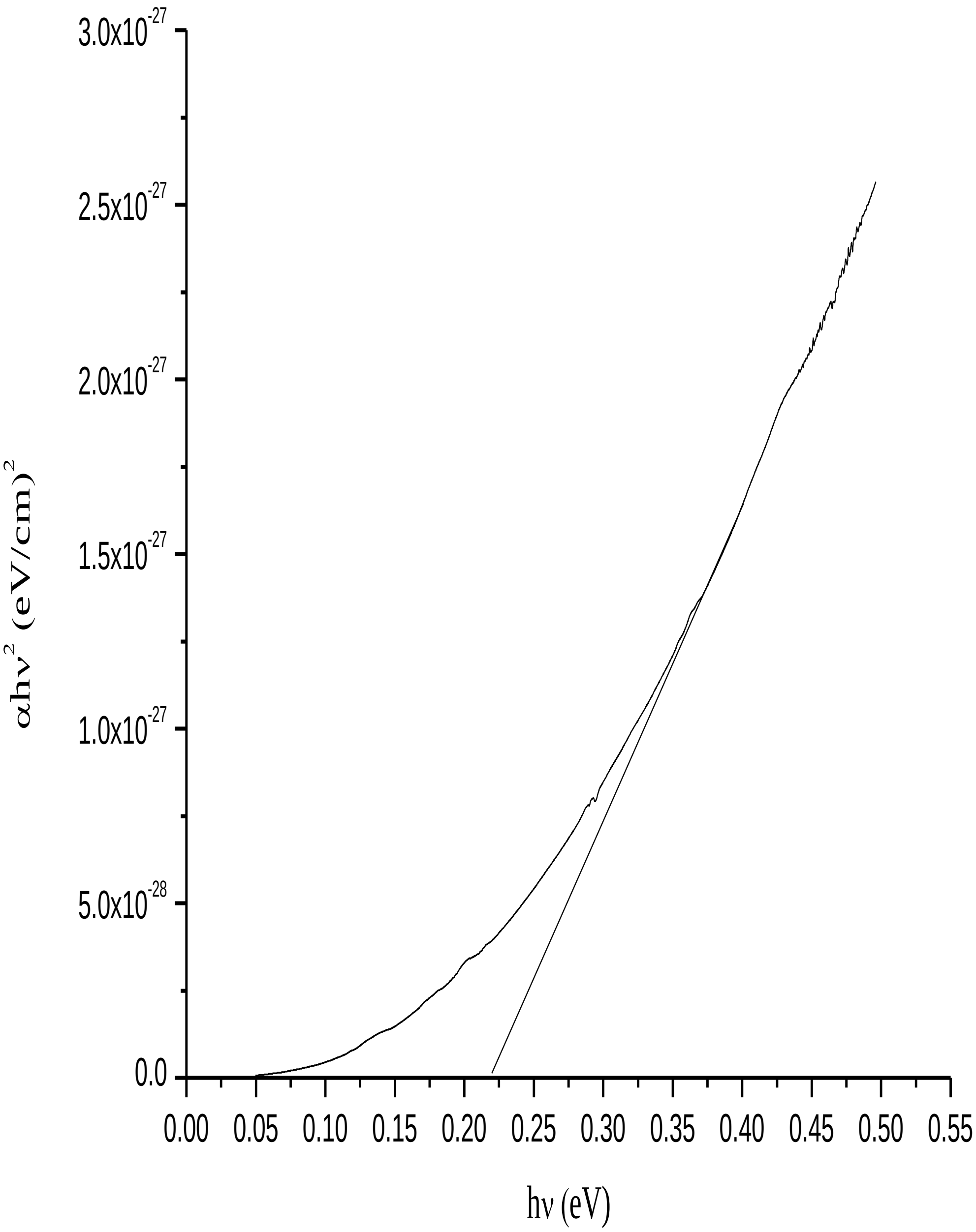

Fig.22 Band Gap of $Bi_{1.8}Sb_{0.2}Te_3$crystals

CONCLUSIONS;

1. Fairly good quality crystals of $Bi_{2-x}SbxTe_3$(x=0, 0.05, 0.1, 0.2) can be obtained by Bridgman-Stockbarger technique at the ampoule lowering rate of 3.5 mm/hr. and temperature gradient around 45°C /cm.
2. In the case of $Bi_{2-x}SbxTe_3$(x=0, 0.05, 0.1, 0.2) single crystal can be obtained by Zone-melting method and the observation on growth features indicates the layer mechanism to be effective in the growth of crystal.
3. There are cellular growth features mechanism due to constitutional supercoolling to effective in the growth of the crystal and stoichiometric deviation of the material due to preferential evaporation of tellurium and also classify the growth of crystals are on (111) plane.
4. EDAX analysis shows that the growth of crystals are stoichiometric and homogenous.
5. The X-ray diffractrometry study indicates the substitution effect of Sb at the bismuth sites in Bi_2Te_3.
6. The band gap of $Bi_2Te_{3,}$ $Bi_{1.95}Sb_{0.05}Te_{3,}$ $Bi_{1.9}Sb_{0.1}Te_{3,}$ and $Bi_{1.8}Sb_{0.2}Te_3$ crystals are about 0.16, 0.18, 0.19 and 0.22 eV (all direct) , respectively. There are no observable indirect transitions in the crystals.

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