Chapter 3: Crystal growth of $InBi_{1-X}Te_X$ Crystals

3.1 Introduction:

Growing an excellent crystal is both an art and a science (Gilman) [1]. Stockbarger grown around 1500 fluorite crystals for military uses in high-quality optical lenses from 1936 to 1949, while Nacken successfully synthesised quartz crystals throughout World War II. It marked the start of the systematic creation of synthetic quartz crystals. Many approaches have been developed to aid in the creation of synthetic crystals. However, the success of the procedures in producing good, pure, and big crystals is dependent on a number of conditions, including: nature of material itself

a) its purity
b) thermal environment
c) the rate of growth
d) pressure
e) diffusion coefficients of the materials
f) impurity concentration and
g) homogeneity

To grow crystals of a given material, a variety of techniques can be employed, and the method used is determined by the properties of the material and application. Laudise [2] has thus provided a systematic taxonomy of growth approaches to simplify this difficulty. The crystal growth process is divided into three categories: Crystal growth is still indeed a subject of art and is a part of the phenomenon of phase change; thus, three specific categories of crystal growth processes can be described [3]:

- Solid Growth (S→S) where solid-solid phase transitions are involved.
- Melt Growth (L→S) where liquid-solid phase transitions are involved.
- Vapour Growth (V→S) where gas-solid phase transitions are involved.

3.2. Crystal growth method:

A brief review of various methods used for crystal growth is given below

- **Crystal growth from solid state:**

Normally, this method is not used and large crystals of a high quality are difficult to obtain, except in certain metals where strain annealing is effective and in certain circumstances when the crystal structure changes between melting and room temperature. A method of forming crystals from polycrystalline ingots by strain annealing at high temperatures that uses the stored energy of deformation as the driving force for crystal growth is known as grain growth.

- **Crystal growth from vapour phase:**

The method can be used for small crystals whose size is not so important. It can produce crystals with great precision. Growth of moderate 4 size bulk crystals with this method has its own theoretical importance. Several researchers evaluated the technique in depth, including Hollnad, Kaldis, Schafer, Nitsche and Wickender et al. [4-8].This methods is sub divided in three categories.

1. **Sublimation:** Sublimation occurs when a suitable temperature is reached. Under proper temperature and pressure conditions, sublimation results in a crystalline solid.
2. **Vapour Transport:** A suitable carrier gas makes the source material volatile and transports it to the crystallization region.
3. **Gas phase reaction:** It is the product of chemical reaction between reactant vapour species, which results in crystal growth from the vapour phase. The crystal growth using vapour phase incurs problem of multi nucleation and hence is not often used to grow large crystals. Although, there are some exceptions such as CdS, ZnSe, Gap, GaAs and Cd_4GeS_6 that can be grown using vapour phase.

➢ Crystal growth from aqueous solution:

Crystallization takes place when the material to be crystallized is dissolved in a solvent or solution to the appropriate concentration. Once the solution has reached the desired saturation point, it is slowly cooled or evaporated. It is possible to grow excellent quality crystals by controlling temperature, humidity and rate of evaporation with a seed crystal. As a result of high solvent solubility and chemical stability requirements, this method has some limitations.

➢ Gel method :

A gel method can be used for growing materials that are not soluble in water, where constituent ions migrate slowly through an inorganic or organic gel, react, and then make the compound. Crystals grown through gel growth show no strain, unlike those formed by melting or vapour. As a result of the compound's concentration exceeding the solubility limit at this point, the crystal nucleates. Because of the size limitation, this method is used only for research. This method has been successful in growing crystals such as TGS, DGS, KCIO4 and others. Henisch has described the method in detail [9].

➢ Hydrothermal growth:

These methods are used to grow crystals of many metals, their oxides, and other compounds that are very poorly or insoluble in water, or that may be soluble in water only at high temperatures and high pressures. A practical challenge with this method is the need for high pressure. It has poor results in terms of size and quality of crystals. A notable exception is the production of piezoelectric quartz crystals for industrial purposes. Ballman et al. [10] and James et al. [11] have discussed this method in detail.

➢ High temperature solution growth :

In this method, high melting point solvents are used, which may be above 600 ^{0}C. It involves many practical difficulties, including choosing the right solvent, chemical and phase stability, high melting points, obtaining high temperatures, contamination and so on, but it is generally used for growing many important materials. It can be used for almost any material that can be dissolved in an appropriate solvent and yields crystals that are more perfect than any other method of crystallization. This method has a very low optimum growth rate. It has been described in detail by Elwell. et al. [12] Examples are YIG, lithium ferrite, gadolinium aluminates, barium titanate, $Ba_2MgGe_2O_7$, ruby emerald etc.

- **Crystal growth from melt:**

A melting process is the most commonly used method for growing large size crystals of metals, alloys, and semiconductors. The method of crystal growth from melt has maximum theoretical importance 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.

As part of the solidification process, heat transfer plays a major role in ensuring growth. Specifically, heat is transferred between solids and liquids through the solid-liquid interface. By eliminating extensive zones of super cooling in the melt, the growing surface can be made stable. Single crystal of Bi, Cd, Sb, Se, Te, Zn, BiSb, SeTe, InBi, SnSe, and $SnSe_2$ have been grown from melt by Bridgeman, Czochralski, Zone melting and Chalmers methods by various 45 workers (Bhatt V. P., Balasuubramaniam, Thattey, Shah B. S., Thakar, Vaishampayan, Pandya, Vyas, Trivedi M. D., Trivedi S. B., Shah R. C. and Gireesan) [13-25].

Zone melting method:

It is a relatively a more efficient method of growth from melt discovered by Pfann [26]. W. G. Pfann at Bell Laboratories in 1951 was pioneer to develop zone refining based on floating zone technique. This technique of floating zone found its direct application in manufacturing of silicon crystal. With further contribution by various researchers and the modifications in the technique it is being applied to grow single crystals of various melting oxides. In this process a polycrystalline crystal is inserted and passed through a heater with a small heating zone. When a narrow region on the crystal is exposed to the heating region the ingot changes its phase to molten state (floating zone). The impurities present in the molten ingot at the liquid-solid interface diffuse from solid region into liquid region and separate out at the end of the ingot after the whole crystal passes through the heater. A seed crystal having a required orientation is brought into contact with the molten region at the beginning of the process in order to re-grow a single crystal.

This process provides advantage of growing high purity crystal where the requirement of high purity crucible is excluded. The process is flexible to grow both congruently and incongruently melting materials. The technique has two important aspects: Impurity removal and uniform distribution of impurity. 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. 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 [27] and Shah [28] 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 [29]. 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 [30-35]. Balazyuk et al [36] 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 [37] have studied the distribution in various layers of $AlxGa1_{-x}Sb$ growing in a temperature gradient field. Shukla et al. [38] have grown $CdBr_2$ single crystals by the zone melting method. Interestingly, Serra et al [39] 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. [40] 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.

3.3 Synthesizing the Compound:

An alloy mixing unit was used in order to make sure a consistent charge for crystal growth, as described in chapter 2. The elements used, viz., Indium, bismuth and tellurium were each of 5N purity purchased from 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 temperature was kept about 50 ºC above the melting point of the alloy, i.e., about 150 ºC. 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 are found sufficient. After this, the molten charge is slowly cooled. This procedure produces fairly homogeneous alloys of $InBi_{1-x}Te_x$(x=0, 0.05, 0.1and 0.15).

3.4 Crystal Growth and surface morphology:

In order to prepare the proposed composition material, the three elements (5N purity) in their stoichiometric proportions were mixed and then sealed in a quartz ampoule under residual pressure ~10^{-5} Pa. The sealed mixture was melted at 150 ºC in a furnace. The molten charge in the ampoule was rocked for 48 hours, for effective homogeneous mixing and compound formation. The proportional controller was used to measure temperature to an accuracy of ±5 ºC, using Chromel-Alumel thermocouple. The zone melting technique of crystal growth was employed to prepare $InBi_{1-x}Te_x$ (x=0, 0.05, 0.1 and 0.15), ~ 60 mm x 8 mm crystals. The samples were processed through ten time to-and-fro passes given for zone levelling at travel speed of 0.3 cm/hr. The temperature gradient of ~45 ºC/cm and having about 0.01 m zone length with zone temperature of about 150 ºC were achieved. The plot of temperature versus distance of the zone melting furnace is given in figure 3.1.

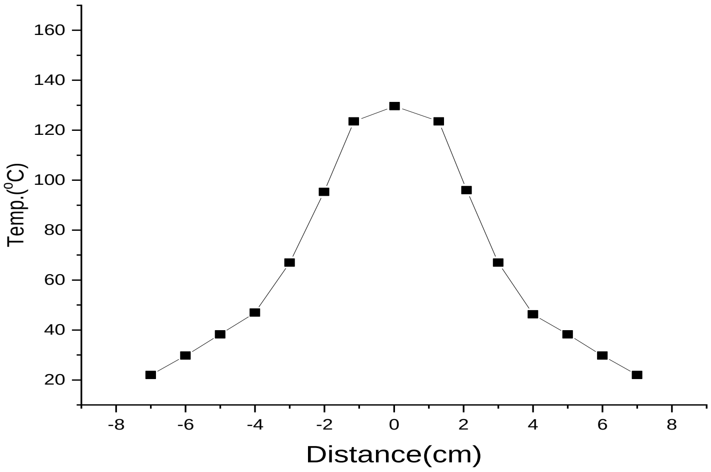


Figure 3.1: Plot of the temperature versus distance in the zone melting furnace.

The single crystal was obtained by using the zone leveled method, as described above, through self-nucleation process. Under optical microscope, freshly cleaved crystal surfaces were observed to have good crystal perfection. Philips X-ray diffractometer (Model PM8203) has been used with radiation $Cu_{k\alpha}$ (λ = 1.5418 Å), for acquiring XRD data from the specimen. The Scanning Electron Microscope of OXFORD Model was used to obtain the composition of the samples from the Energy Dispersive Analyzer by X-ray (EDAX) data.

The study of crystal forms is defined as crystal morphology. The morphology of minerals is primarily concerned with the external features of matter, but the structure of a crystal, including its formation, surfaces, cleavage cracks and other surface features are also included by crystal morphology. In addition to providing an indication of internal crystal perfection, surface morphology is also a link to internal of the crystal surface.

Various crystallographic features have been observed on crystal surfaces of metals, semiconductors, and their alloys that are as-grown. These features describe the crystal growth conditions [41-44]. Mourizone et al. observed features in the form of striations in InSb crystals. [45]. It was recognized that these striations are due to impurities, and not due to orientations or growth rates that depend on convection currents in the melt. Researchers, Teghtsoonian and Chalmers also observed striations parallel to the growth axis which they attributed to cellular structure at the solid-liquid interface [46]. Bhatt et al.[47-48] in the case of Bi-Sb alloy crystals, observed striations on the free surface of the as- grown crystals as well as triangular and hexagonal crystallographic features on the cleavage plane. Based on their findings, they concluded the striations in the material are caused by growth anisotropy caused by dendritic growth which changes with alloy composition.

In the case of $InBi_{1-x}Te_x$ (x=0, 0.05, 0.10 and 0.15) crystals obtained using Zone melting method, no growth features have so far been reported. However, the present author has observed some interesting features on the as-grown crystals. The top free surfaces of the as-grown crystals observed under optical microscope exhibited parallel striations in the case of $InBi_{0.95}Te_{0.05}$ crystal as shown in Fig. 3.2, implying layer mechanism of crystal growth that is common to melt growth in general.

Figure 3.2: Striation in the case of $InBi_{0.95}Te_{0.05}$

Fig. 3.3 shows a crystal grown having length 60 mm and diameter 8 mm. The overall appearances of all the crystals grown were similar. The doped as well as pure crystals were observed to have fairly good luster.

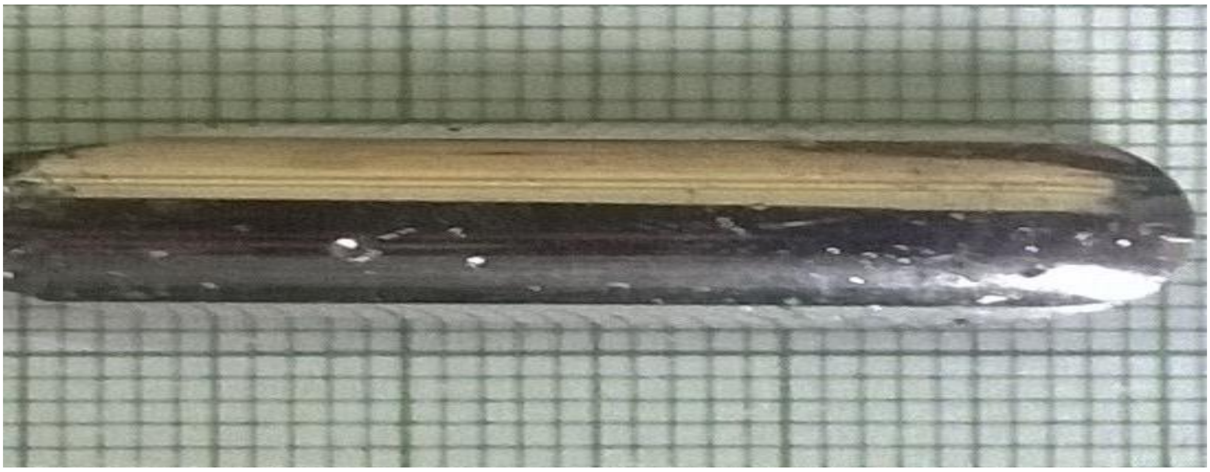


Figure 3.3: As grown crystal of $InBi_{0.90}Te_{0.10}$

3.5 X-Ray diffraction analysis:

The study of bulk and thin films materials X-ray diffraction techniques can be useful for structural studies. Powder XRD has become an indispensable method for structural characterization of materials. It is a non-destructive technique for analyzing a wide range of specimens such as plastics, metals, minerals, semiconductors and ceramics. Shah et al., [47 - 50] have used metallographic techniques in conjunction with X-ray powder diffractions pattern to assess the homogeneity of pseudo-binary and ternary alloys.

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. The intensity of the diffracted beam is automatically plotted using a recorder as the counter moves on a goniometer circle which is in synchronization with the specimen over the selected range of 2θ value.

Typical X-ray data diffraction spectra of $InBi_{1-x}Te_x$ (x =0, 0.05, 0.10 and 0.15), crystal powders are shown in Figures 3.4 - 3.7, respectively. The pattern consists of well-defined sharp diffraction lines indicating good crystallinity of the crystals. The identification of peaks in diffraction intensity was made using a JCPDS [ASTM-JCPDS card no. 32-0113] [51]. 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. Table 3.1 shows the lattice parameters values of the c and a, evaluated from the X-ray data.

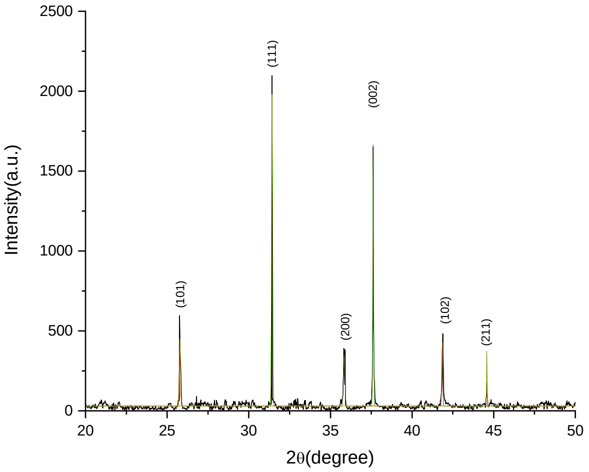


Figure 3.4: The XRD Plot of InBi

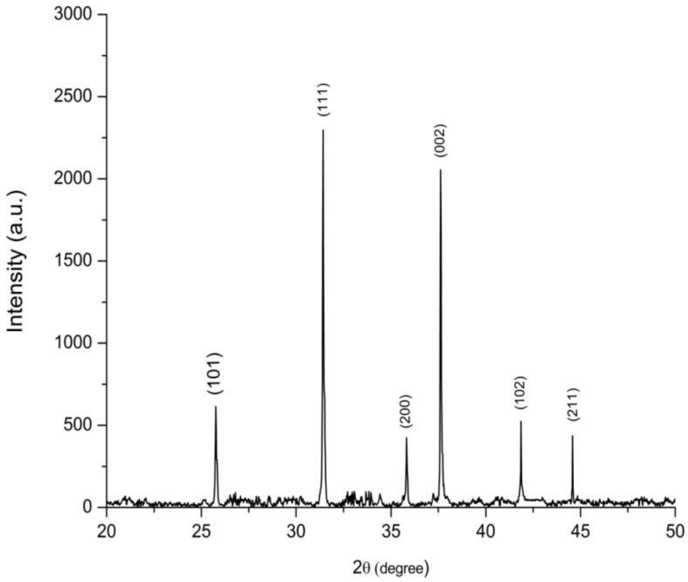


Figure 3.5: The XRD Plot of $InBi_{0.95}Te_{0.05}$

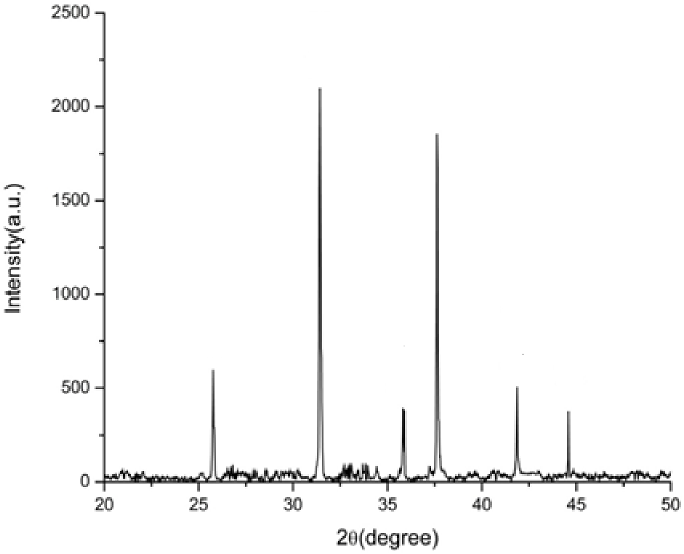


Figure 3.6: The XRD Plot of $InBi_{0.90}Te_{0.10}$

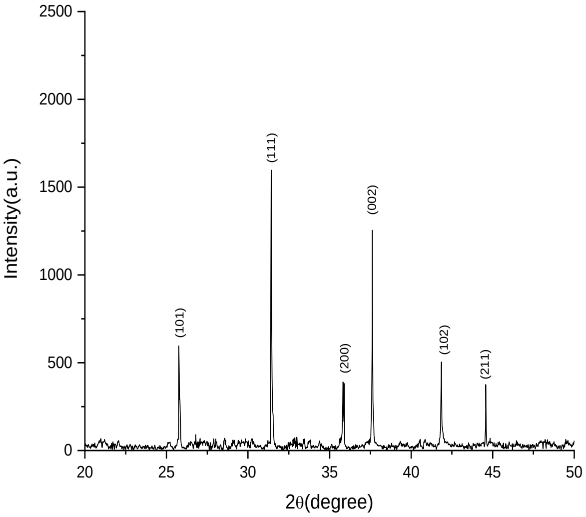


Figure 3.7: The XRD Plot of $InBi_{0.85}Te_{0.15}$

Table 3.1: Lattice parameter of $InBi_{1-x}Te_x$ (x=0, 0.05, 0.10, 0.15)

Crystal	a (Å)	c (Å)
InBi	4.9894	4.7835
$InBi_{0.95}Te_{0.05}$	4.9892	4.7833
$InBi_{0.90}Te_{0.10}$	4.9893	4.7829
$InBi_{0.85}Te_{0.15}$	4.9894	4.7827

3.6 Crystallite size:

The crystallite size is an important parameter as the sizes of the crystals determine whether the material is soft (small crystallites) or brittle (large crystallites). The crystal grain size can be quantitatively calculated by Debye Scherrer equation according to the diffraction peak broadening in the XRD curves. Actually, the results calculated by theDebye Scherrer equation are the thickness perpendicular to the crystal planes. Debye Scherrer equation for the calculation of particle size is

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where K is the Scherrer constant (0.98), λ is wave length of the X-ray beam used (1.5418 Å), β is the Full width at half maximum (FWHM) of the peak and θ is the Bragg angle. Scherrer constant denotes the shape of the particle and its value is most commonly taken as 0.98. Scherrer equation accounts for broadening solely due to crystallite size [51-56]. Crystallite size (D) is extracted from the high intensity peaks of sample using Debye Scherrer equation giving the average size to be 47.17 nm and strain to be 1.64 $x10^{-3}$.

3.7 Energy Dispersive Analysis of X-rays:

An energy dispersive X-ray spectrometer (EDS or EDX) provides information about a sample's chemical composition by analyzing the reflected energy. From the EDAX data one can ensure the stoichiometry and purity of the crystals [57]. The change in stoichiometry of the melt occurs when the vapour pressure and reactivity of group VI elements are different from those of group III-IV. Additionally, this changes the other properties of the crystal. The present study concentrates on the detection and quantitative and distributional analysis of the components present in the Zone melting grown crystals, viz., $InBi_{1-x}Te_x$ (x = 0, 0.05, 0.1 and 0.15). Figure 3.8 show the FESEM and EDAX for InBi crystal. Figures 3.9-3.14 show the FESEM, EDAX and the color mapping for $InBi_{0.95}Te_{0.05}$, $InBi_{0.90}Te_{0.10}$ and $InBi_{0.85}Te_{0.15}$ crystals, respectively. Figures 3.9 (a-c), 3.11 (a-c) and 3.13 (a-c) show the FESEM images of the crystals $InBi_{0.95}Te_{0.05}$, $InBi_{0.90}Te_{0.10}$ and $InBi_{0.85}Te_{0.15}$ implying the material growing into smooth layer growth mode with planar surfaces of good perfection. The EDAX spectra for all the crystals could provide a qualitative overview about the elemental composition. In support of EDAX, the color mapping of all the crystal was studied for better qualitative and quantitative evaluation of the elements. The atomic percentages in In, Bi, Te, in $InBi_{1-x}Te_x$ (x=0, 0.05, 0.1 and0.15) as obtained from EDAX are mentioned in Table 3.2. It can be observed that the samples have quite satisfactory stoichiometric compositions.

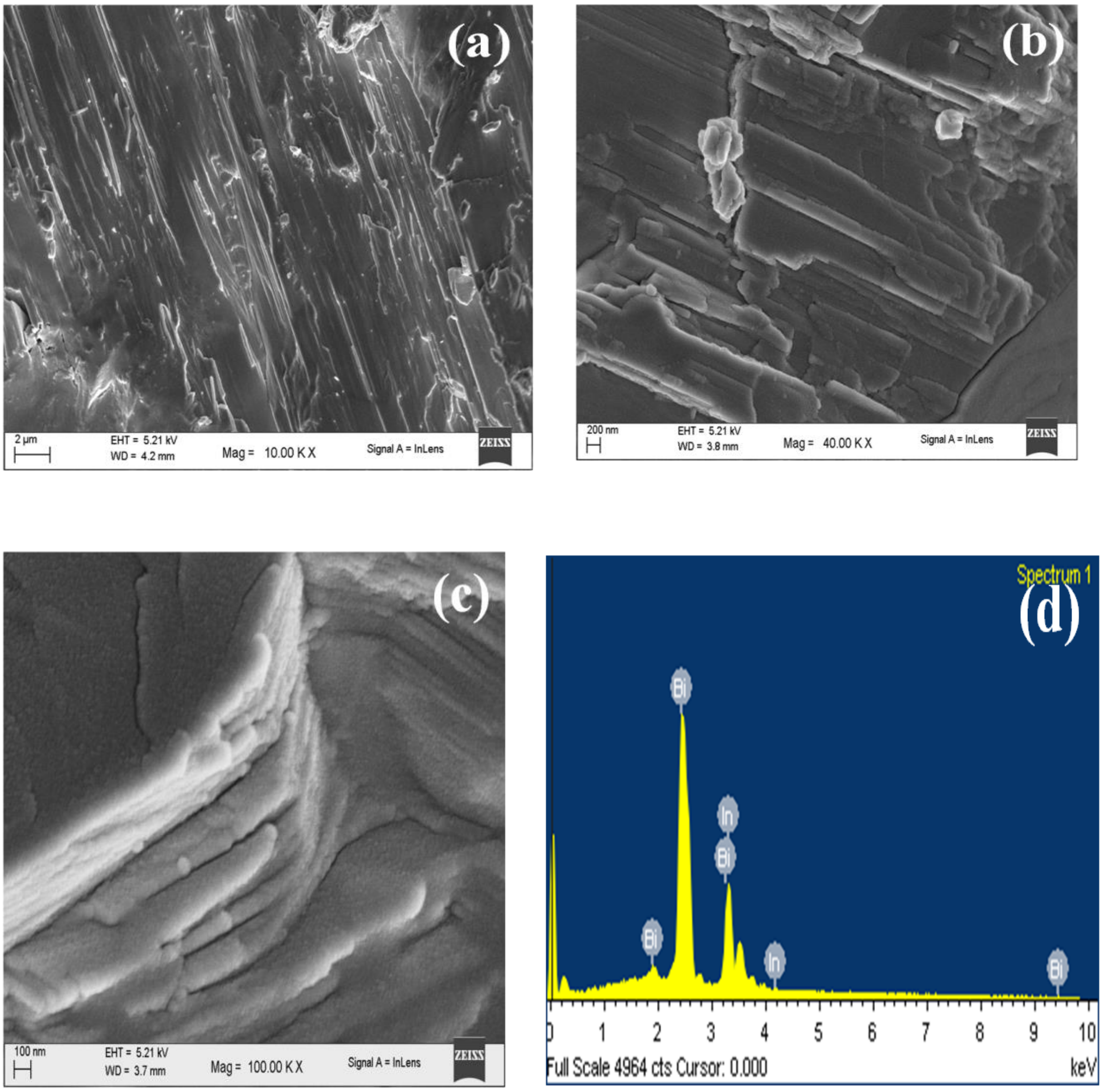


Figure 3.8 (a-c): FESEM images and **(d)** Energy dispersive spectra of InBi crystal, respectively.

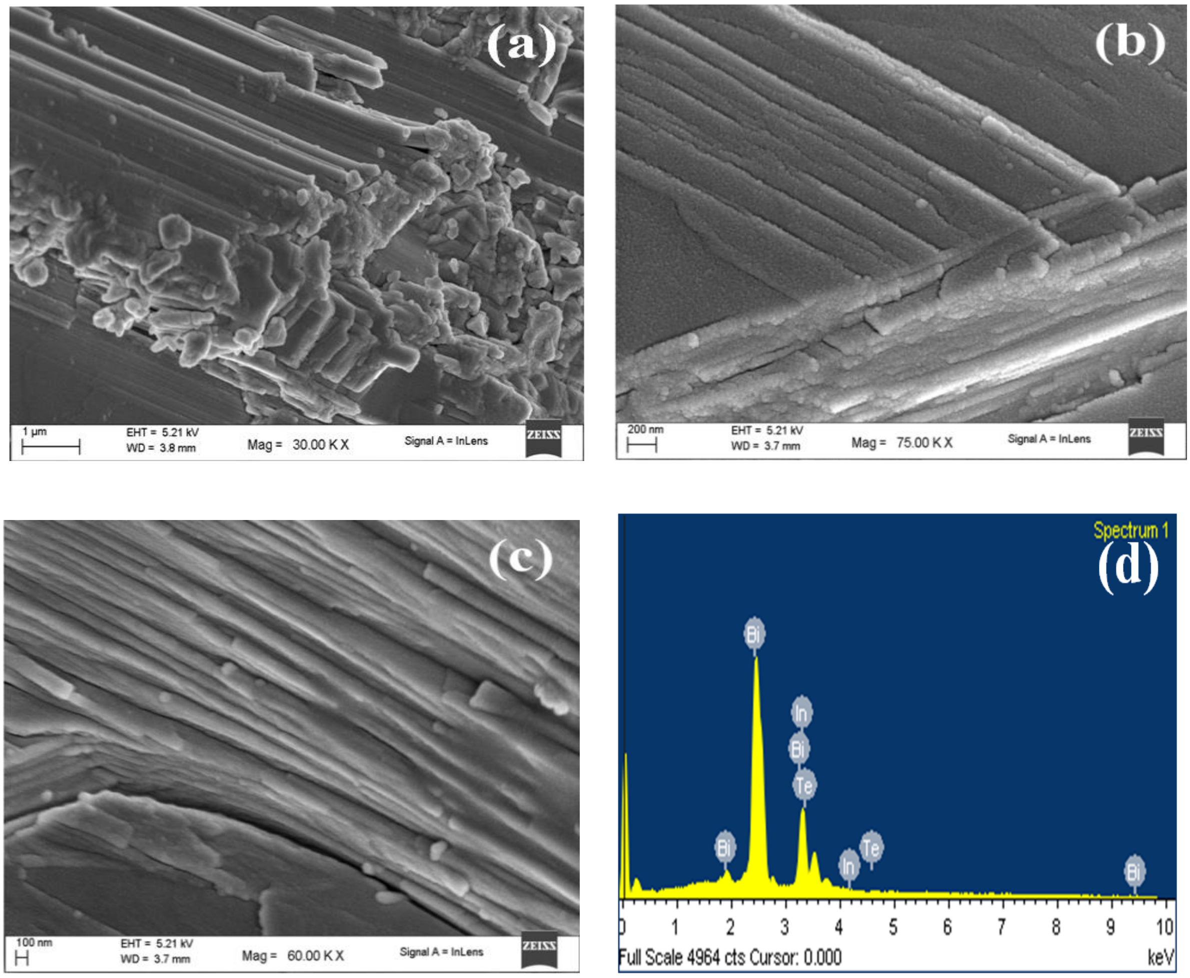


Figure 3.9 (a-c): FESEM images and **(d)** Energy dispersive spectra of $InBi_{0.95}Te_{0.05}$ crystal, respectively.

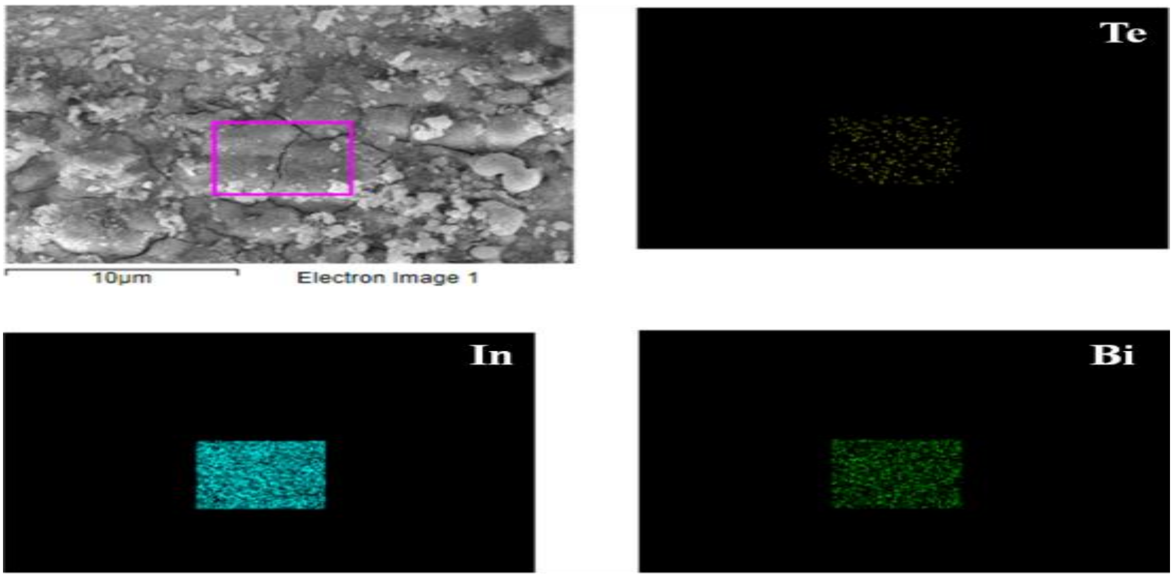
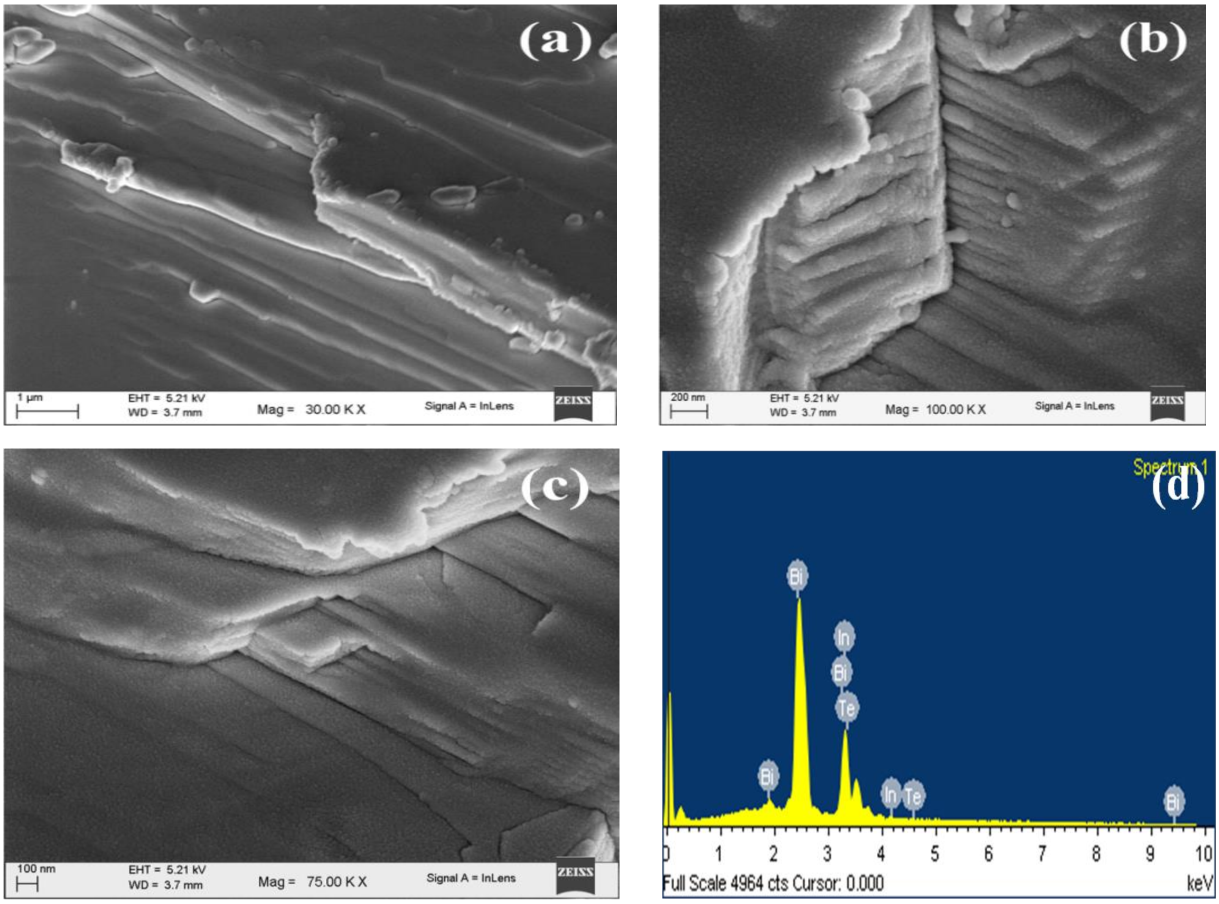


Figure 3.10: Color mapping of $InBi_{0.95}Te_{0.05}$ crystal, respectively**.**



Figures 3.11(a-c): FESEM images and **(d)** Energy dispersive spectra of InBi$_{0.90}$Te$_{0.10,}$ crystal, respectively.

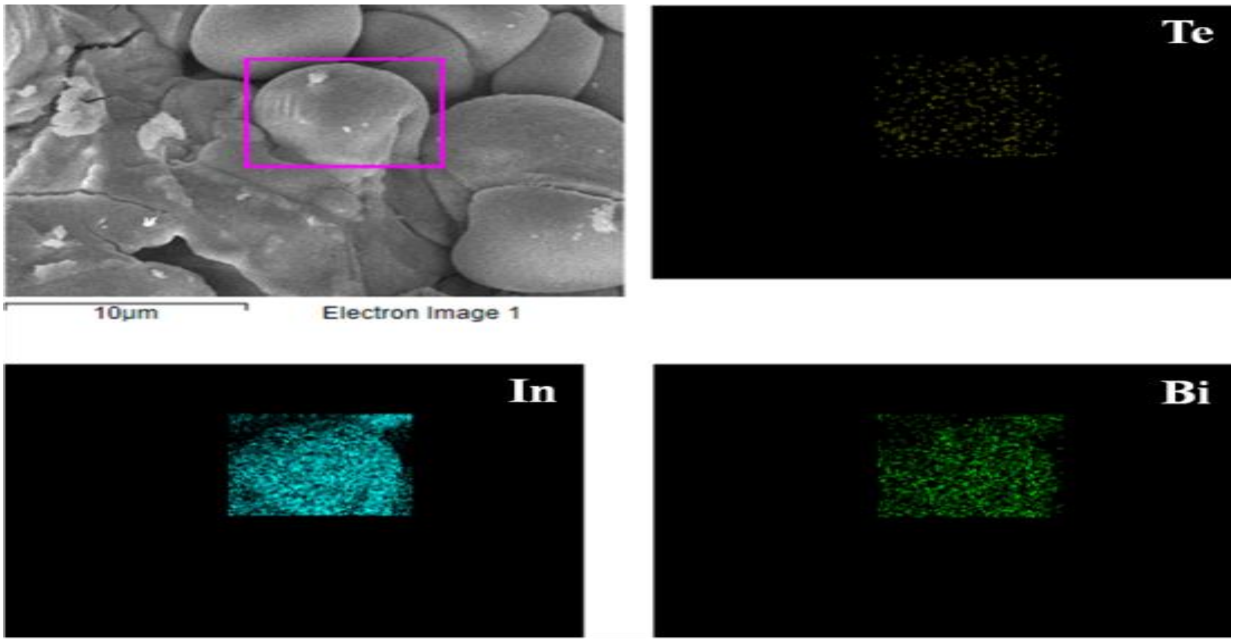
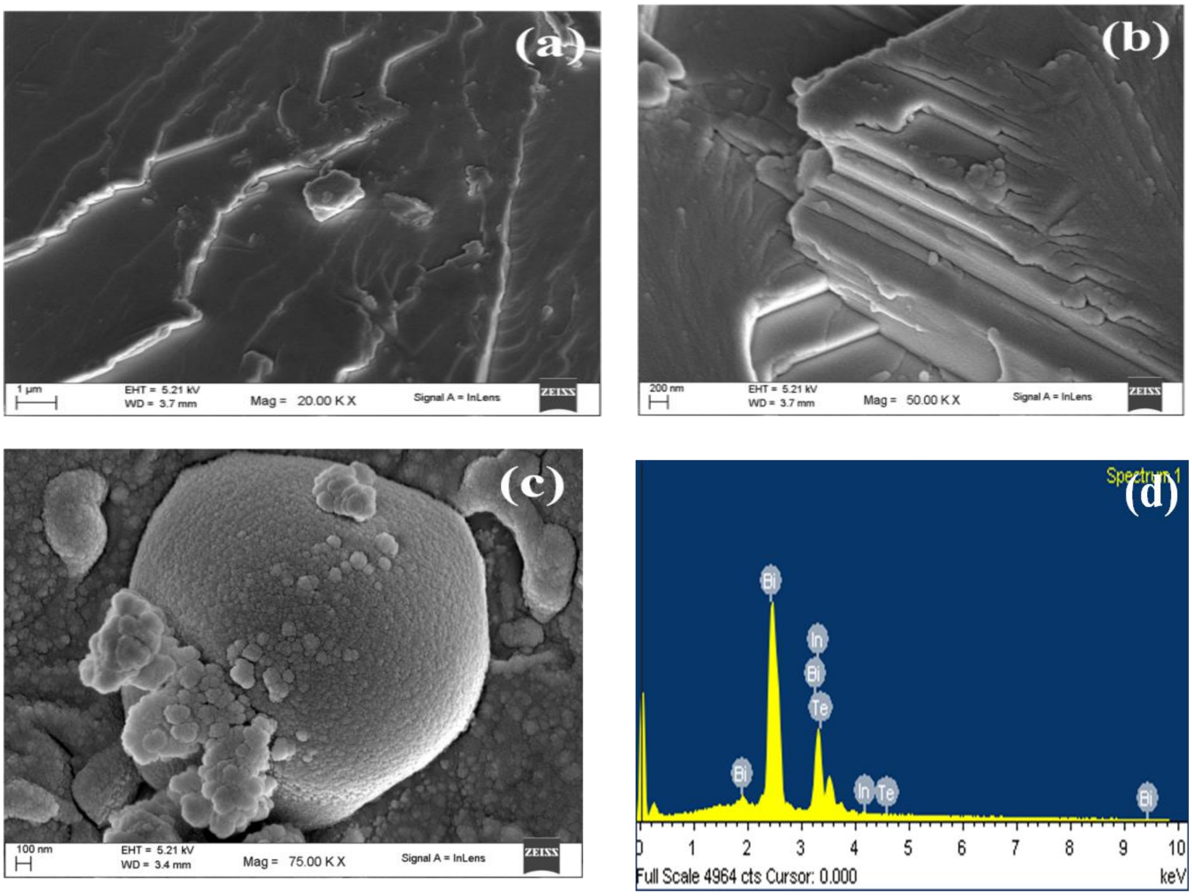


Figure 3.12. Color mapping of InBi$_{0.90}$Te$_{0.10}$ crystal, respectively**.**



Figures 3.13(a-c): FESEM images and **(d)** Energy dispersive spectra of $InBi_{0.85}Te_{0.15}$, crystal, respectively.

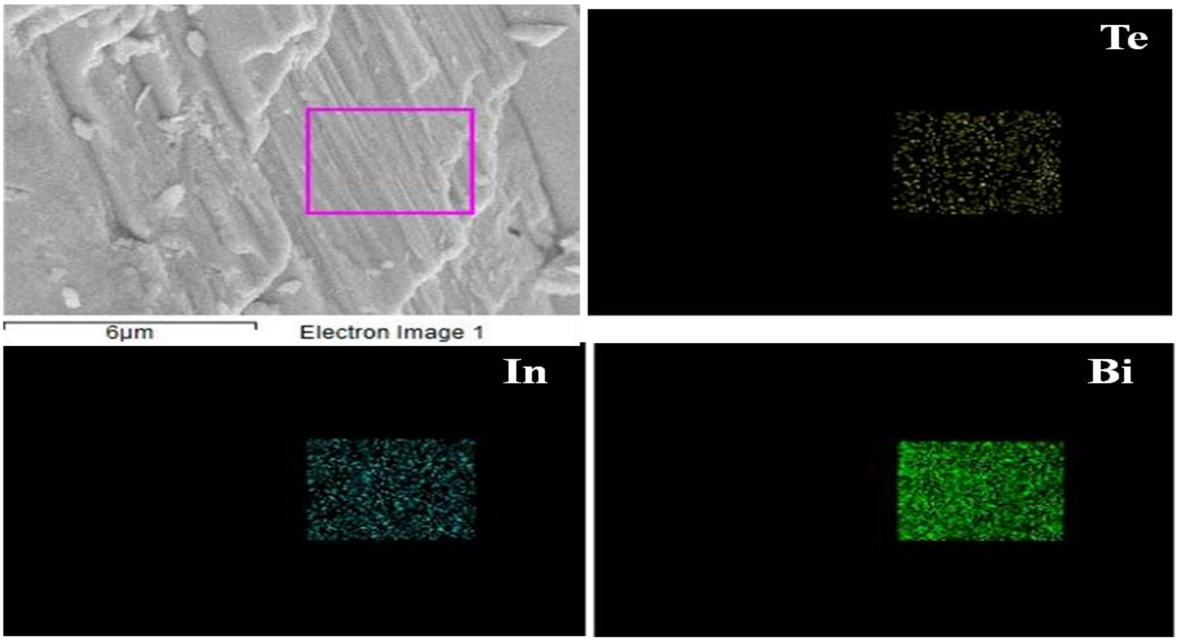


Figure 3.14 Color mapping of $InBi_{0.85}Te_{0.15}$ crystal, respectively**.**

Table 3.2.

The elemental compositions as analyzed in three different regions of $InBi_{1-x}Te_x$ (x=0.00,0.05,0.010 and 0.15) crystal.

Crystal	Element Present	Atomic (%)
InBi	In Bi Te	35.08 64.92 0.00
$InBi_{0.95}Te_{0.05}$	In Bi Te	35.80 62.73 1.47
$InBi_{0.90}Te_{0.10}$	In Bi Te	36.42 59.56 4.02
$InBi_{0.85}Te_{0.15}$	In Bi Te	36.80 57.06 6.14

In order to avoid the plastic strain, the freshly grown crystal was cleaved along the basal plane at 0℃. The ingot obtained after zone-melting was cleaved at various places. The crystal has easy cleavage along the plane (001). It was found that the cleavage surface exhibits constant orientation along the length of the crystal, which indicates the ingot is a single crystal. No misorientation on the cleaved surface of the crystal was observed under an optical microscope, implying very good macroscopic perfection.

3.8 Conclusions:

Zone-melting method can be successfully used to grow single crystals of $InBi_{1-x}Te_x$ (x=0.00,0.05,0.010 and 0.15) with following important conclusions that can be drawn from this study:

1. The InBi crystals possess high crystalline nature as confirmed from the XRD analysis. The lattice parameter *a* remained almost constant while *c* showed monotonic decrease with the increase in concentration of the dopant Te.
2. The process permits proper stoichiometric doping of the Te at Bi site in the grown crystals as confirmed by EDAX analysis.
3. The synthesized crystals were observed to be free from any major surface defects as examined using FESEM images.

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