CHAPTER: 3

CRYSTAL GROWTH AND PHYSICAL PROPERTIES OF $InSb_{1-X}Bi_x$ (x=0.00, 0.03, 0.04, 0.05) CRYSTALS AND THIN FILMS

I. CRYSTAL GROWTH

To grow a good crystal is an art as well as a science (Gilman) [1]. During 1936 to 1949, Stockbarger grew about 1500 flourite crystals for military applications in high-quality optical lenses and Nacken successfully synthesized quartz crystals during the second world war. It was beginning of the systematic growth of synthetic quartz crystals. For the growth of synthetic crystals, there are many techniques developed. However, the success of the techniques in obtaining good, pure and large crystals depends on various factors:

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

A variety of processes can be used to grow crystals of a given material, and the approach chosen relies on the material qualities and application. Hence a systematic classification of growth techniques to simplify this problem has been given by Laudise [2]. There are three basic categories of the crystal growth process:

1) Solid growth: S---S this process involves solid phase transitions.
2) Vapour growth: V---S this process involves gas-solid phase transitions.
3) Melt growth: L---S this process involving liquid- solid phase transitions.

The present chapter give a brief review of various methods used for crystal growth.

1.1Crystal growth from solid state:

Except for some metals where strain annealing is efficient and in specific circumstances when a crystal structural change occurs between the melting point and room temperature, this approach is rarely used, and good quality crystals of great size are rarely formed. 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.

1.2Crystal 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 size bulk crystals. The technique has been reviewed thoroughly by Holland, Kaldis, Schafer, Nitsche and Wickender et al [3-7]. 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 by 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 multi-nucleation. There are some exceptions such as CdS, ZnSe, Gap, GaAs and Cd_4GeS_6.

1.3 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 supersaturation. 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 limitation of this method for its application to other materials is the requirements of high solubility and chemical stability of solution.

1.4 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 form 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 is only 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 method has been discussed in detail by Henisch [8].

1.5 Hydrothermal growth:

Crystals of many metals, their oxides and other compounds 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. The method has been discussed in details by Ballman et al [9] and James et al [10].

1.6 High temperature solution growth:

This method is used for the solvents having high melting point, may be above 600°C. 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., many important materials are being grown by this method. Examples are YIG, lithium ferrite, gadolinium aluminate, 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 higher 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 [11].

II. CRYSTAL GROWTH FROM MELT:

Crystal growth from melt is the most useful method due to the high growth rates obtainable. Numerous variants in this category exist and mainly involve the details of the geometry of the liquid–solid interface. The chances of impurity inclusion during the crystal growth from melt can be reduced with special efforts. Moreover, the crystal can be doped with a desired impurity to a desired concentration. Crystals of metals, metallic alloys, semiconductors, superconductors, ionic solids and alkali halides can be grown from melt. 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.

The principles of the crystal growth from melt are based on cooling of a liquid (i.e. melt) to solidification in a controlled manner. The solidification process should be so controlled as to promote extension of a single nucleus without producing new nuclei and with minimum of chemical and structural disorder in the growing crystal. By avoiding zones of super-cooling in the melt the formation of a new nucleus and instability of the growing surface can be eliminated.

The method involves the transfer of heat through the solid liquid interface. The heat transfer can be given by the equation.

$$K_s G_s - K_L G_L = LV$$

where,

K_s = thermal conductivity of solid

K_L= thermal conductivity of liquid

Gs= temperature gradient in solid

G_L= temperature gradient in liquid

L= latent heat of fusion per unit volume

V = growth velocity

Hence many parameters affect the growth process such as the temperature gradient, the growth velocity and the composition of molten charge. In the case of alloys, if a concentration gradient is established in the liquid during growth, there results non-uniform composition of constituents in the alloy crystal and also the constitutional super-cooling. The composition of frozen material in such cases is always different from the liquid or the molten charge. The instability of interface occurs and cellular structure results (Tiller et al [12]). Delves[13] has shown that the constitutional super-cooling can be reduced to minimum, by having slow growth rate, by stirring the melt to minimise solute concentration gradient and by having a steep temperature gradient. In the case of growth of a single crystal from a doped material or a non-congruently melting alloy, the solute transport plays an important role in addition to heat transport in the success of the growth process. During crystal growth in such cases, solute segregation occurs at the solid-liquid interface due to unequal equilibrium solute concentration in solid to that in liquid. In most of the alloy systems, K<1. The solute segregation may occur due to,

(i) Crystals with non-uniform solute distribution along the length of the crystal and

(ii) Constitutional super-cooling.

The concept of constitutional super-cooling was introduced by Rutter et al [14]. The result of constitutional super cooling is the instability of the interface giving rise to cellular structure, dendritic structure, stray nucleation, waviness of interface etc., spoiling the quality of the crystal

obtained. Further, Delves [13] has defined a parameter "S" known as constitutional super-cooling parameter given by,

$$S=\frac{mG_{LS}}{G_L}$$

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.

G_L = temperature gradient in liquid

It has been shown that if S > 1, constitutional super-cooling will occur. Thus, the chances of constitutional super-cooling can be reduced by using slow growth rate, good stirring of the melt to minimise G_{LS} and using steep temperature gradient.

The crystal growth from melt can be pictured as an atom-to-atom addition to the lattice similar to the growth from vapour and the experimental evidences rule out the necessity of a screw dislocation to promote the growth of metal crystals from melt. This has been concluded from a number of observations. Firstly, Dash [15] has successfully grown large areas of single crystals of silicon, free from dislocations. A few other metal crystals have also been grown without observable dislocations. Secondly, if the dislocations are necessary to promote growth, the high symmetry of the dendritic growth cannot be accounted. Hence the conclusion of nucleation at the re-entrant edge of a screw dislocation is not so important for the growth of metal crystals from melt. Chalmers et al [16] have proposed a step-like interface which provides permanent re-entrant steps which are not propagated by dislocations and evidences for the existence of such steps have been obtained.

Most of the investigations in the field of crystal growth from melt were aimed at,

(i) study of the morphology of the interface and the effect of the various growth parameters on it.

(ii) study of the substructures observed on the crystal grown from melt.

(iii) study of imperfection, their formation and distribution in the crystals and

(iv) study of preferred orientation and the influence of various parameters responsible for this property of crystals.

Many crystals have been grown from melt by various workers and many reviews have been published (Gilman, Holden, Maritus, Hurale, Honeycomb, Winegard, Lawson et al, Hilsum et al, Hannay, Tannenabaum, Smakula, White, Laudise et al, Elbaum and Brice) [1,17-30].

There are three basic techniques for crystal growth from melt:

(1) Bridgman method

(2) Czochralski method and

(3) Zone melting method

A short account of these methods is given below.

2.1 Bridgman-Stockbarger Method:

This method of growing crystals was first developed by Bridgman [31] in 1925. In this technique, the melt is kept in a suitable container and moved relative to a fixed temperature gradient in a vertical furnace so that the solidification starts from one end proceeds gradually to the other end of the sample. The tip of the container entering the freezing temperature zone is made conical in shape so that initially only a small volume of the melt is super-cooled which results in the formation of only one nucleus having suitable orientation and finally a single crystal is obtained.

A modification of this method was successfully done by Stockbarger using two furnaces at different temperatures and separated by a baffle, instead of using a single furnace, this modified method is known as Bridgman-Stockbarger method and provides for desired variation of the temperature gradient.

The limitation of Bridgman method is that, it can be used only for the low melting point metals, which is overcome by the horizontal moving furnace technique given by Chalmers [32].

The Bridgman method has been most frequently applied for three types of materials:

(a) Metals [33-35]

(b) Semiconductors [36-37]

(c) Alkali and Alkaline earth halides [38-39]

As per the specific requirements posed by the nature of materials, the technique has been developed into a sophisticated one. For example, Kamagawa et al [40] have grown $InSb_{1-x}Bi_x$ ($x < 0.03$) and $In_xGa_{1-x}Sb$ ($x < 0.01$) ternary mixed crystals on InSb and GaSb seed crystals successfully by the Bridgman method with high speed rotation of about 80 to 120 r.p.m. Fang-Lang Hsu[41] has reported the growth of $(Sb_xBi_{1-x})_2Te_3$ single crystals with programmable temperature control by horizontal two zone Bridgman furnace in quartz ampoules evacuated to as low pressure as 30×10^{-7} torr. Voda et al [42] have grown pure and doped. CdF_2 single crystals by the Bridgman method wherein unwanted vapour reactions were avoided by using an argon atmosphere and glassy carbon crucibles.

2.2 Czochralski Method:

A popular method of crystal growth from melt was developed by Czochralski [43] in 1918. This method is also known as Kyropoulos [44] method or the crystal pulling method. By this method the crystals with large size and relatively low dislocation density can be grown in a very short time. The main advantage of this method is that the size and diameter of the crystal can be controlled during the crystal growth process.

In this method, the material which is to be grown is melted in a crucible. Seed crystal is then dipped slightly, rotated and slowly pulled from the melt. During rotation, the melt is stirred to attain thermal symmetry. The excess heat is then removed by conduction through the seed holder. The essential factors for obtaining good crystals are,

a) Accurate control of temperature,

b) Pulling rate and

c) Rate of rotation

Here the diameter of the growing crystal depends on the temperature and the pulling rate but it is limited by the diameter of the crucible. The principles of the method have been discussed by Gilman [1] and Brice [30]. The practical aspects of this method have been discussed in detail by Draper [45]. The technique has reached hi-tech status due to its applicability for technologically important materials.

Laudise et al [46] have grown doped single crystals of Bi_2Te_3 by Czochralski method in H_2 and in inert atmospheres. Wenzle et al [47] have grown copper crystals by Czochralski method in a hydrogen atmosphere at a pressure of 1 bar.

2.3 Zone Melting Method:

The zone melting method of crystal growth from melt was invented by Pfann [48] in 1952. In this method a small molten zone is created in a large solid ingot of the material to crystallize and 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 the temperature gradient. The smaller the zone length, the better is the quality of the crystal.

Impurity removal:

The method which 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, is known as zone refining process. Here various impurities are collected at the two ends of the ingot (depending on their segregation coefficient). In this process, the impurities with segregation coefficients $K>1$, are collected at the father end. The portion between the two ends of the ingot can be obtained purer after each successive zone pass.

Uniform doping of impurity:

The impurity distribution in an ingot doped with a known impurity can be made uniform by the process known as zone-levelling. In this process, a molten zone is repeatedly passed through the length of the ingot in alternate directions. After several alternate repeated passes, the segregation of the dopant can be virtually eliminated which results in the homogeneous distribution of impurity in the ingot.

Discontinuous bands of impurity such as in a p-n junction, are often required in the fabrication of semiconductor devices. This can be efficiently done by the zone melting technique. The theoretical and practical aspects of this method describing various modifications are discussed in detail by Parr [49] and Shah [50]. Herington [51] has reviewed the technique with particular reference to organic compounds. This method has been widely used to grow crystals and to refine various materials by different workers, e.g. Herman et al. Richards Delves, Hamaker et al, Brower et al and Swineheart [52-57]. The crystals like InBi and Bi-Sb, have been grown in this laboratory using zone melting method by previous investigators Bhatt et al and Shah et al [58-60].

Balazyuk et al [61] have grown cadmium antimonide and zinc antimonide single crystals by the zone melting method to study the effect of crystal growth condition on the structural perfection and thermal properties. Lunin et al [62] have studied the distribution of AlSb in varizone layers of $Al_xGa_{1-x}Sb$ growing in a temperature gradient field. Shukla et al [63] have grown $CdBr_2$ single crystals by the zone melting method. Serra et al [64] have successfully grown large area zinc sheet single crystals by using a modified zone melting method. This is a hybrid of the zone melting and the horizontal Bridgman techniques. Fan Zhanguo et al [65] have used the zone melting method for preparing YBaCuO superconductor successfully.

Lostak et al [66] have grown $Bi_{2-x}In_xSe_3$ (x= 0.00 to 0.66) single crystals using a modified Bridgman method. The crystal homogeneity was studied by determining the indium content and the variations of Seeback coefficient in the directions perpendicular and parallel to the crystal axis. Subramanian et al [67] have grown ternary mixed $InBi_2Te_4$ crystals and obtained semiconducting polycrystalline ingots. Jansa et al [68] have successfully grown $Bi_{2-x}In_xTe_3$ crystals (x = 0.1) by Bridgman method.

Sagar et al [69] have grown Bi_2Te_3 crystals by Bridgeman method and Arivoulli et al [70] have grown Bi_2Te_3 crystals by vapour phase technique. Kutasov et al [71] have grown $Bi_2Te_{2.8}Se_{0.2}$crystals bysolid solution. Laudise et al [72] have grown doped single crystals of $Bi_2Te_3$by Czocharlski method in H_2.

Single crystal of Bi, Cd, Sb, Se, Te, Zn, Bi-Sb, Se-Te, In-Bi, SnSe, and $SnSe_2$ have been growth from melt by Bridgeman, Czochralski, zone melting and Chalmers methods by various

workers (Bhatt et al, Bhatt, Balasuubramaniam, Thattey, Shah B. S., Thakar, Vaishampayan, Pandya, Vyas, Trivedi M. D., Trivedi S. B., Shah R. C. and Gireesan) [73-85].

There is no report of growth studies on $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals. The present study is mainly concentrated on the Bridgeman method.

III. CRYSTAL GROWTH OF$InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) CRYSTALS.

Indium, antimony and bismuth each of 5N purity were purchased from sigma Aldrich India. The stoichiometric amounts of all the ingredients were weighed correctly up to 10 micrograms using a semi-microbalance and then placed in a quartz ampoule of about 10 cm in length and 1 cm in diameter. The quartz tube was then vacuum sealed at a pressure of 10^{-4} Pa (to prevent material oxidation) and kept in the alloy mixing furnace. The material was mixed in the molten form in this mixing unit for around 48 hours at a temperature of 577 °C by rotating the tube at 10 rpm. The material was then kept in a molten condition for another 24 hours to accomplish homogeneity and complete reaction in the molten charge. It was then gently cooled to room temperature, after this procedure usually an alloy results is quite homogenous.

The temperature was measured and controlled with a proportional temperature controller within ± 5 °C using Chromel-Alumel thermocouple. For crystal growth by the Bridgeman method, the ampoule with the ingot was kept in the vertical Bridgeman furnace. The temperature profile of the furnace is shown in Figure A. The length of the core of the furnace was about 45 cm. A baffle was kept at 23 cm, i.e., between the two halves of the furnace. The inner diameter of the core was 5 cm. The upper furnace was kept at 577°C, i.e.,~ 50°C higher than the melting point and the lower furnace was set to optimum temp was 107°C well below melting point of the material. The ampoule was kept steady for 24 hours in the upper hot zone of the furnace and was solidified at steady lowering rates in the range of 1mm/hr and temperature gradients about 45°C/cm (Figure – A). The crystals obtained were about 3 cm in length and 1 cm in diameter. They could be cleaved easily. Microscopically the cleavage plane of the crystal was found to be fairly planar.

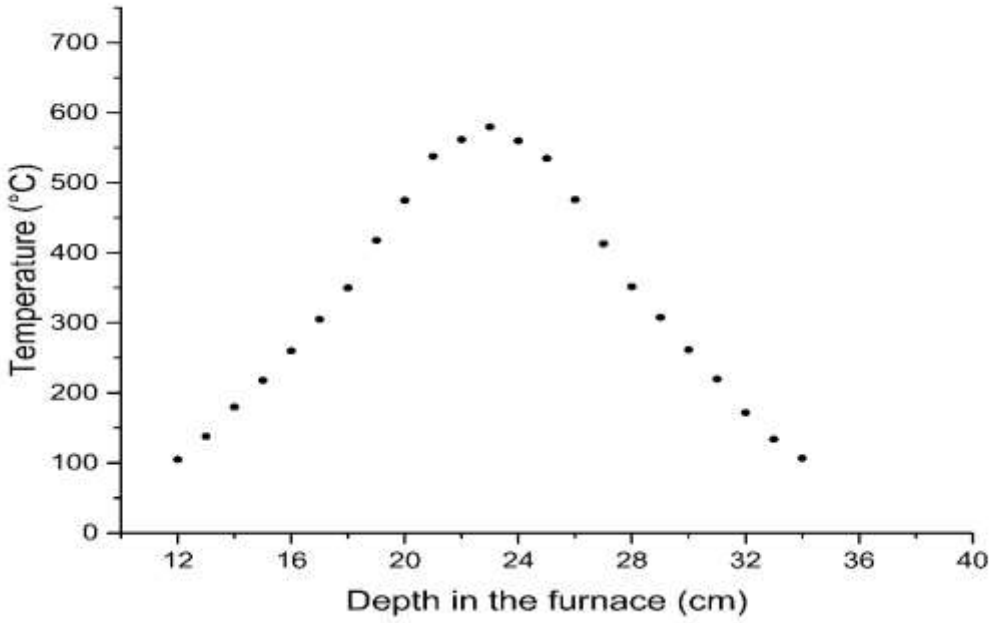

Figure – A temperature profile of the Bridgeman - Stockbarger furnace

3.1 EDAX characterization:

The EDAX analysis was carried out on $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals grown. EDAX data analysis were performed on highlighted portion shown in figures. From the EDAX data one can ensure the stoichiometry and purity of the crystals [86].The calculated and obtained weight percentages of the constituent elements are enlisted in table-1. Figures 1, 2, 3 and 4 shows the elemental mapping. From the mapping images the homogenous distribution of elements were observed. The figures show that the uniform distribution of In, Sb, and Bi throughout the crystals.

Table-1: Standard and observed weight percentages of elements obtained from EDAX

Samples	Standard Weight %			Observed Weight %		
	Indium	Antimony	Bismuth	Indium	Antimony	Bismuth
InSb	48.53	51.47	-	48.64	51.36	-
$InSb_{0.97}Bi_{0.03}$	48.01	49.37	2.62	48.11	49.41	2.48
$InSb_{0.96}Bi_{0.04}$	47.83	48.69	3.48	47.91	48.45	3.64
$InSb_{0.95}Bi_{0.05}$	47.65	48.01	4.34	47.55	48.02	4.43

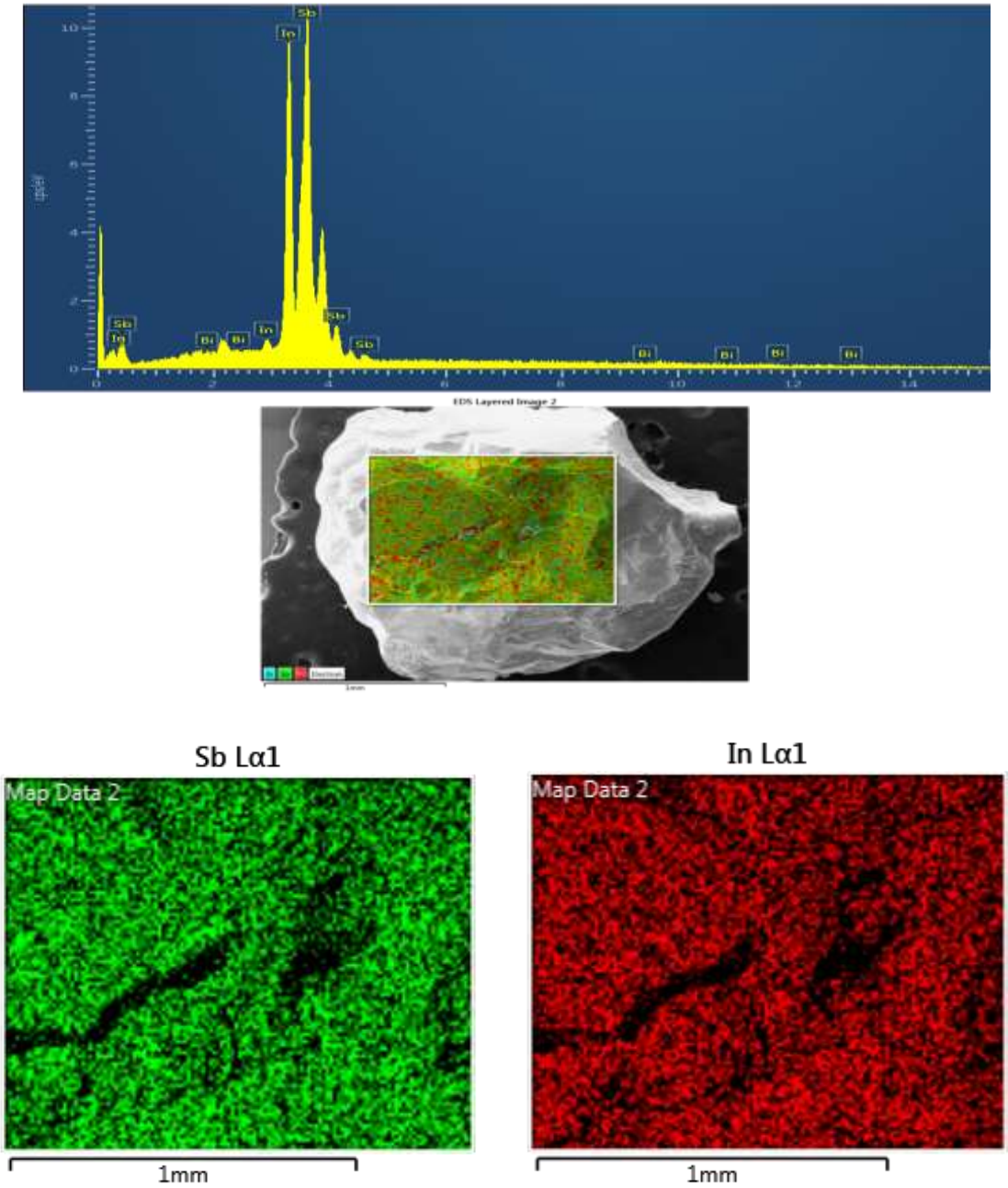

Figure – 1 EDAX and elemental mapping of InSb crystals

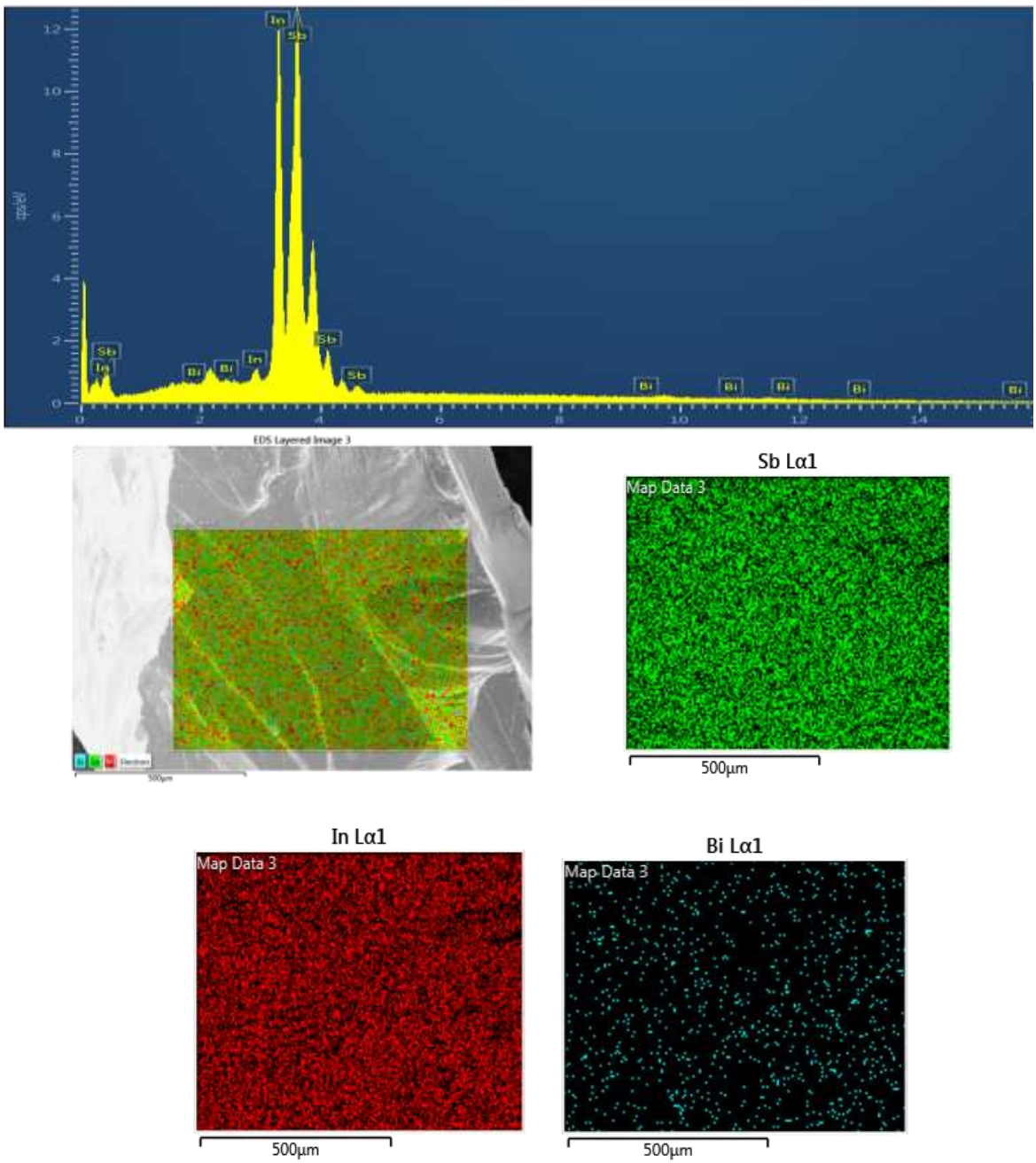

Figure – 2 EDAX and elemental mapping of $InSb_{0.97}Bi_{0.03}$ crystals

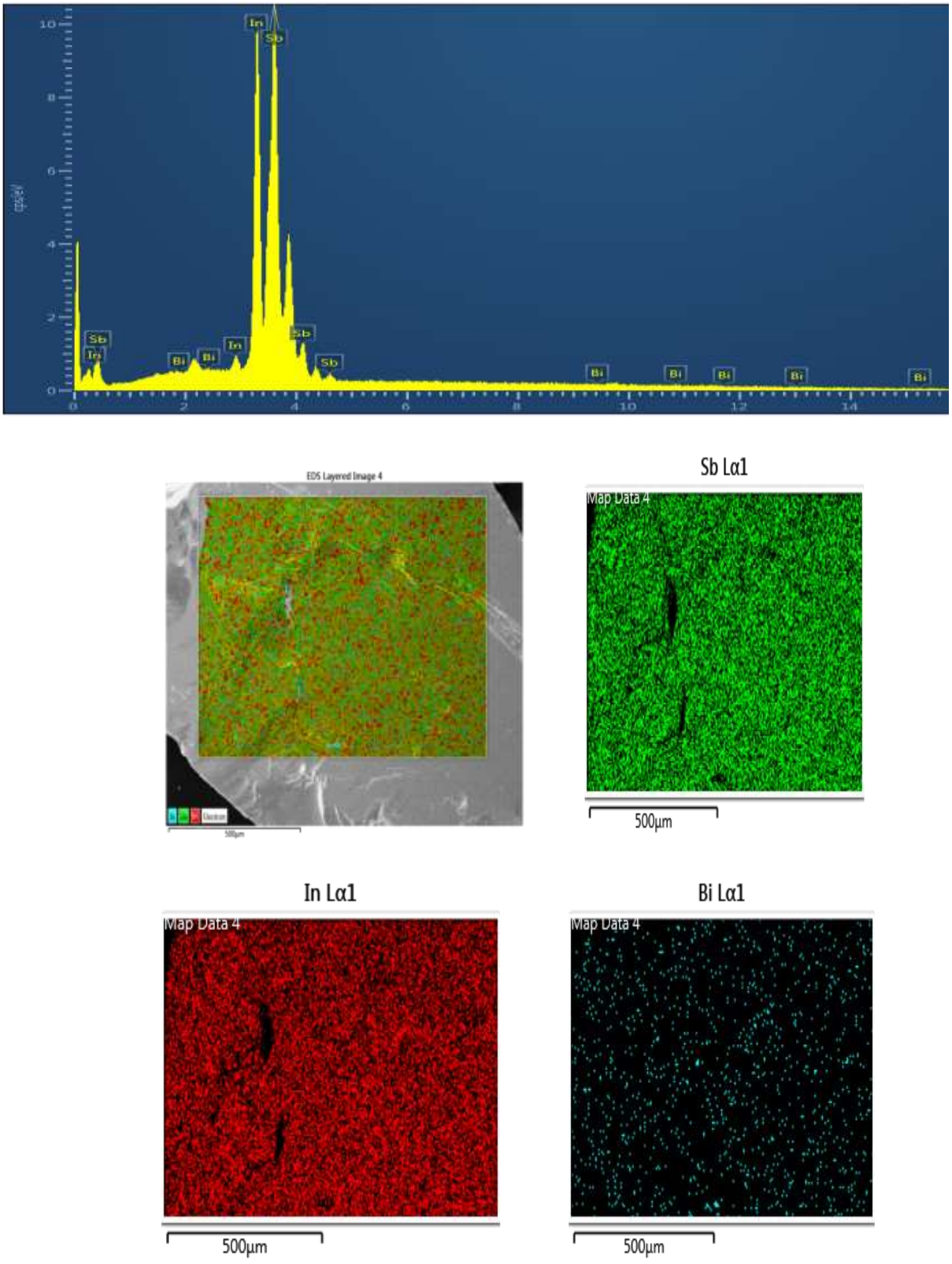

Figure – 3 EDAX and elemental mapping of $InSb_{0.96}Bi_{0.04}$ crystals

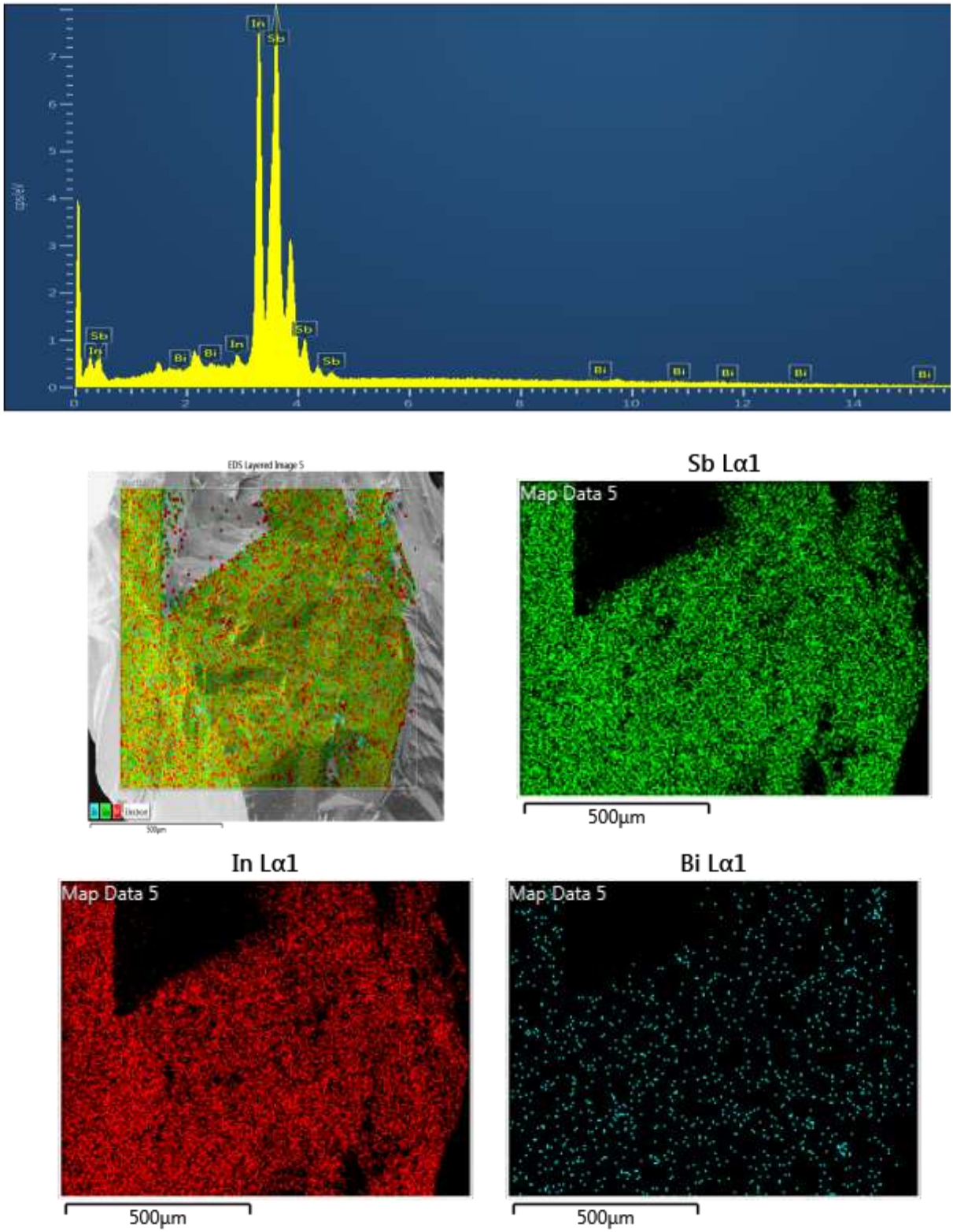

Figure – 4 EDAX and elemental mapping of $InSb_{0.95}Bi_{0.05}$ crystals

3.2 X-ray diffraction

For X-ray diffraction characterization, powdered samples from different parts of the crystal were used to obtain X-ray diffractograms. For this, Bruker D8 Advance X-ray Diffractometer was used with $CuK\alpha_1$ (λ = 1.54056 Å) radiation. The typical diffractograms of $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystalsare shown in figures 5, 6, 7 and 8, respectively. The patterns consist of well-defined sharp diffraction lines indicating good crystallinity of the specimens. The JCPDS data cards were used to identify the peaks in diffraction spectra [87]. On the prominent peaks in the relevant figures, the compound and index assignments are marked. The d-values in the observed and JCPDS files are found to be quite similar. $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals have a cubic structure and face centered lattice having space group $F\bar{4}3m$ [88-89].

The peaks observed in XRD plot(figure – 5) obtained for InSb crystal at 23.76°, 39.35°, 46.64° and 56.94° correspond to (111), (220), (311) and (400) InSb reflections, respectively, (ASTM-JCPDS card no. 06-0208 and card no. 73-1985).

The peaks observed in XRD plot (figure – 6) obtained for $InSb_{0.97}Bi_{0.03}$ crystal at 23.74°, 39.21°, 46.63°, 56.86°,62.60°, 71.54° and 76.41° correspond to (111), (220), (311), (400), (331), (422) and (511) InSb reflections, respectively, (ASTM-JCPDS card no. 06-0208 and card no. 73-1985).

The peaks observed in XRD plot (figure – 7) obtained for $InSb_{0.96}Bi_{0.04}$ crystal at 23.61°, 39.34°, 46.51°, 56.73°,62.34°, 71.30° and 76.28° correspond to (111), (220), (311), (400), (331), (422) and (511) InSb reflections, respectively, (ASTM-JCPDS card no. 06-0208 and card no. 73-1985).

The peaks observed in XRD plot (figure – 8) obtained for $InSb_{0.95}Bi_{0.05}$crystal at 23.87°, 39.46°, 46.63° and 57.12° correspond to (111), (220), (311) and (400) InSb reflections, respectively, (ASTM-JCPDS card no. 06-0208 and card no. 73-1985).

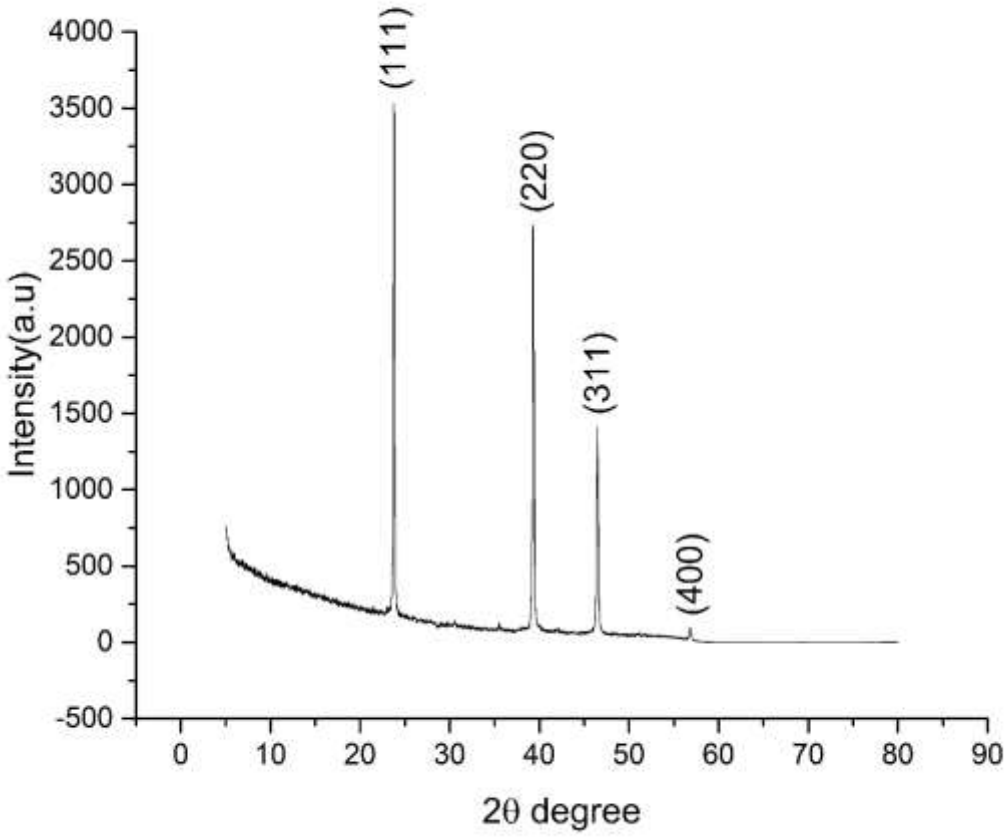

Figure - 5 X-ray diffractogram of InSb crystal

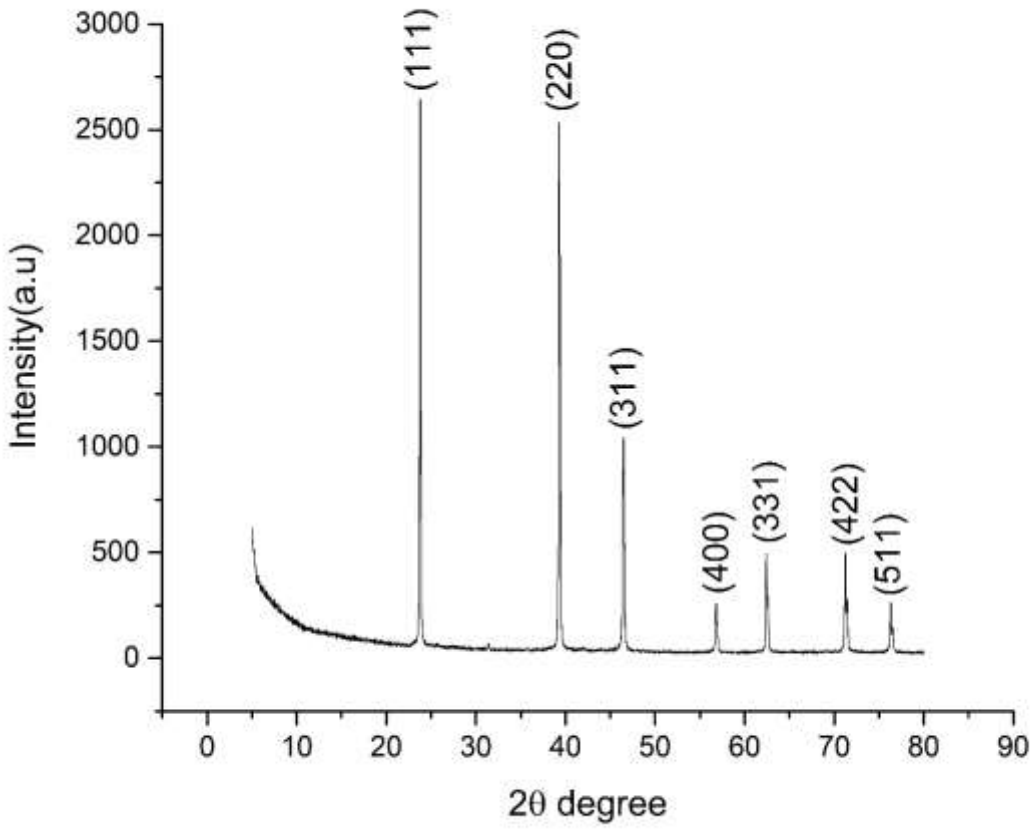

Figure - 6 X-ray diffractogram of $InSb_{0.97}Bi_{0.03}$ crystal

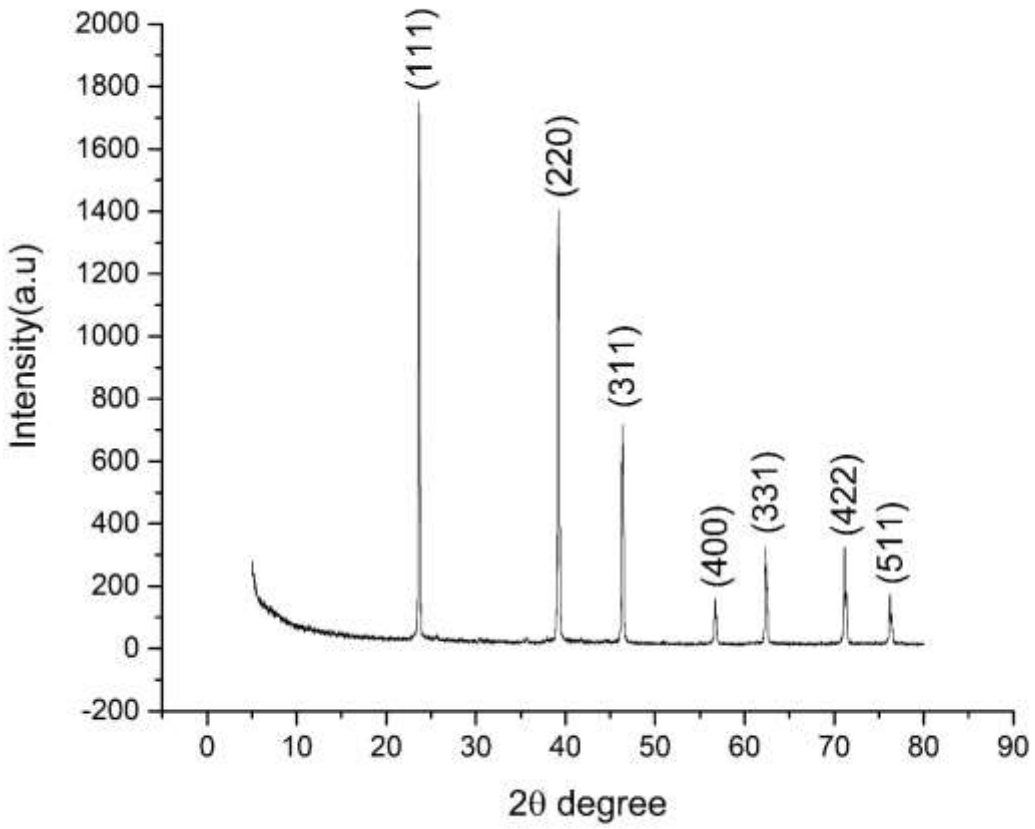

Figure - 7 X-ray diffractogram of $InSb_{0.96}Bi_{0.04}$ crystal

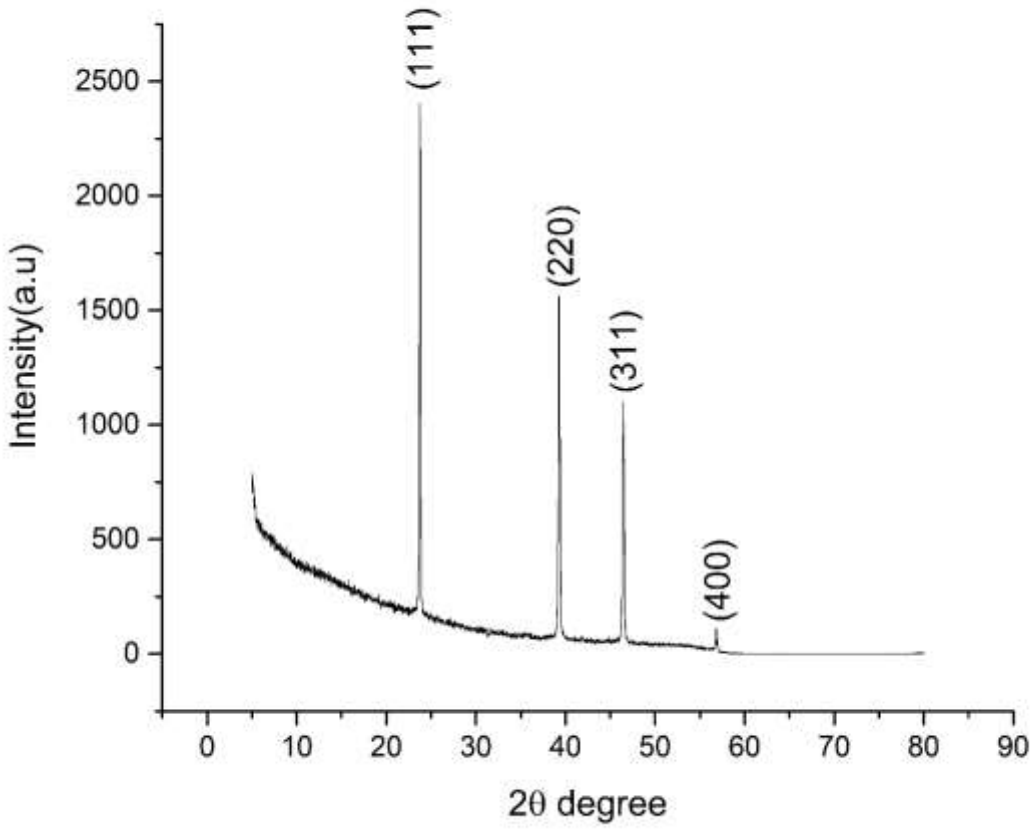

Figure - 8 X-ray diffractogram of $InSb_{0.95}Bi_{0.05}$ crystal

The typical diffractograms of $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) thin films are shown in Figures 9, 10, 11 and 12, respectively. In the XRD plot obtained for InSb thin film (figure 9), peaks are observed at 32.97° and 67.20° corresponding to (020) and (040) InSb reflections, respectively, (ASTM JCPDS card no. 22-0066) [90].

In the XRD plot obtained for $InSb_{0.97}Bi_{0.03}$ thin film (figure 10), peaks are observed at 23.76°, 63.12° and 71.90° corresponding to (111), (331) and (422) InSb reflections, respectively, (ASTM JCPDS card no. 73-1985). The peak at 31.84° corresponds to (020) InSb reflection (ASTM-JCPDS card no. 71-1309) [91], whereas the 48.54° peak corresponds to (113) Bi reflection (ASTM JCPDS card no. 02-0592) [92].

In the XRD plot obtained for $InSb_{0.96}Bi_{0.04}$ thin film (figure 11), peaks observed at 24.62° and 46.20° correspond to (111) and (311) InSb reflections, respectively, (ASTM JCPDS card no. 73-1985) while the one at 32.40° corresponds to the (020) InSb reflection (ASTM JCPDS card no. 22-006).

In the XRD plot obtained for $InSb_{0.95}Bi_{0.05}$ thin film (figure 12), the peak observed at 24.40° is associated with the (111) reflection (ASTM JCPDS card no. 73-1985) and peaks at 31.72°, 33.38° and 67.62° are associated with the (020), (011) and (040) InSb reflections, respectively, (ASTM JCPDS card no. 22-0066).

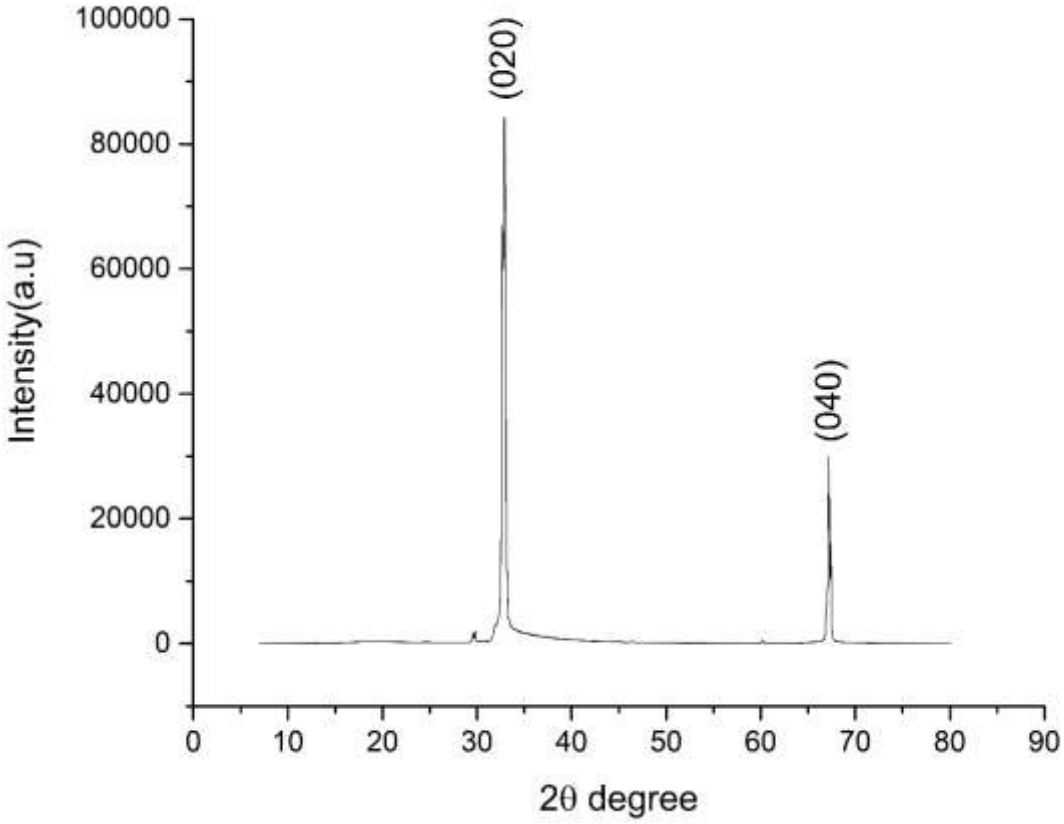

Figure - 9 X-ray diffractogram of InSb thin film

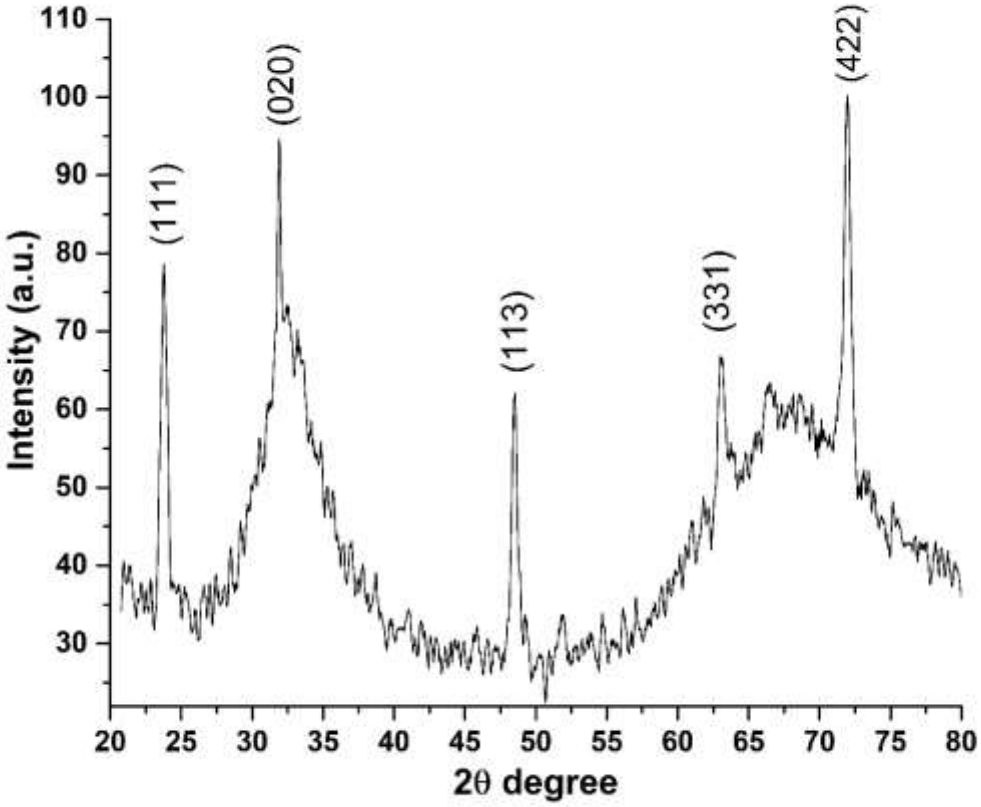

Figure - 10 X-ray diffractogram of $InSb_{0.97}Bi_{0.03}$ thin film

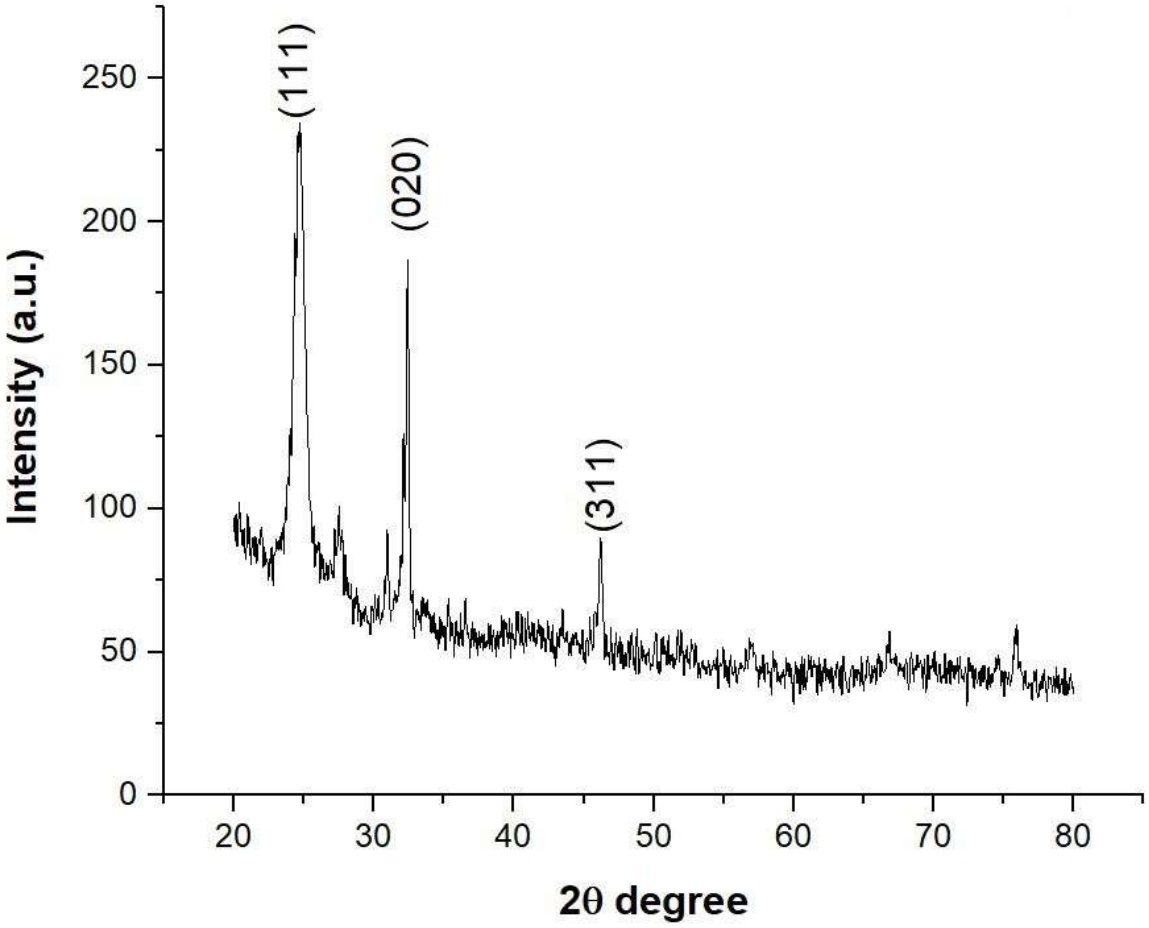

Figure - 11 X-ray diffractogram of $InSb_{0.96}Bi_{0.04}$ thin film

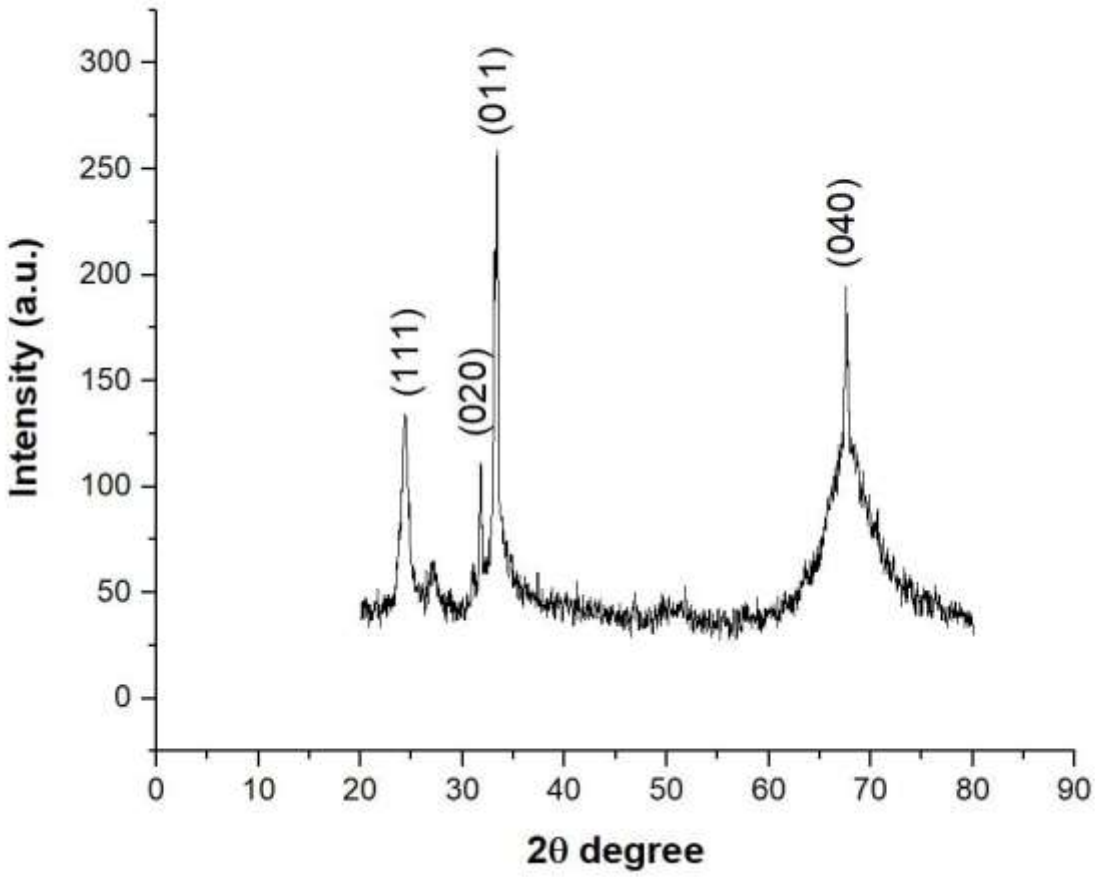

Figure - 12 X-ray diffractogram of $InSb_{0.95}Bi_{0.05}$ thin film

3.3 Hall measurement:

The Hall measurements were carried out at room temperature using the Van der Pauw method [93]. Two opposite probes were connected to a power supply with a digital current meter in series and across the other two probe, a digital microvoltmeter was connected to measure the voltage. The crystal was placed between the poles of a strong electromagnet giving a field of about 18K gauss maximum. The current and voltage were measured with and without the magnetic field. A large number of samples were measured at room temperature. The Hall coefficient, mobility and carrier concentration of $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals are listed in table - 2. The Hall coefficient was found to be positive indicating that the majority charge carries are holes.

Table-2: Hall coefficient, mobility and carrier concentration of $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals

Crystals	Hall Co-efficient $(\frac{cm^3}{coul})$	Carrier mobility $(\frac{cm^2}{V\,sec})$	Carrier concentration 10^{18} cm^{-3}
InSb	2.5570	21552	2.4443
$InSb_{0.97}Bi_{0.03}$	4.8948	11080	1.2769
$InSb_{0.96}Bi_{0.04}$	4.9201	6275	1.2703
$InSb_{0.95}Bi_{0.05}$	2.5929	8405	2.4104

3.4 Thermoelectric power characterization:

The thermoelectric power measurement was carried out on freshly cleaved surfaces of $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) single crystals, using differential temperature method. The temperature difference between the hot and cold junctions was kept at 5K. The measurement was carried out in the temperature range from 300K to 500K. The sign of thermal EMF and the results of the hot probe tests show that the $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals are all of p-type, in agreement with the Hall coefficient results. Figures 13, 14, 15 and 16 give the plots of the thermoelectric power versus temperature, obtained for the $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals, respectively. The plots indicate that thermoelectric power increases exponentially

with increasing temperature, agreeing with the behaviour expected of a typical degenerate semiconductor [94].

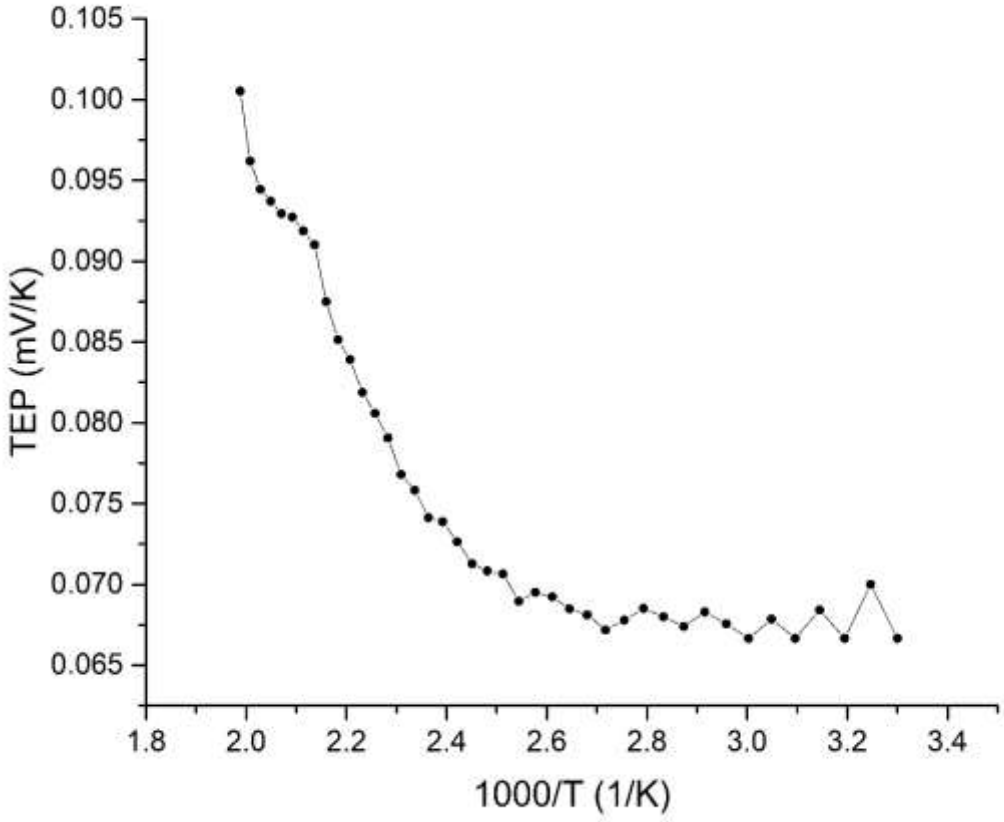

Figure - 13 plots of the Thermoelectric power versus Inverse of Temperature for InSb crystal

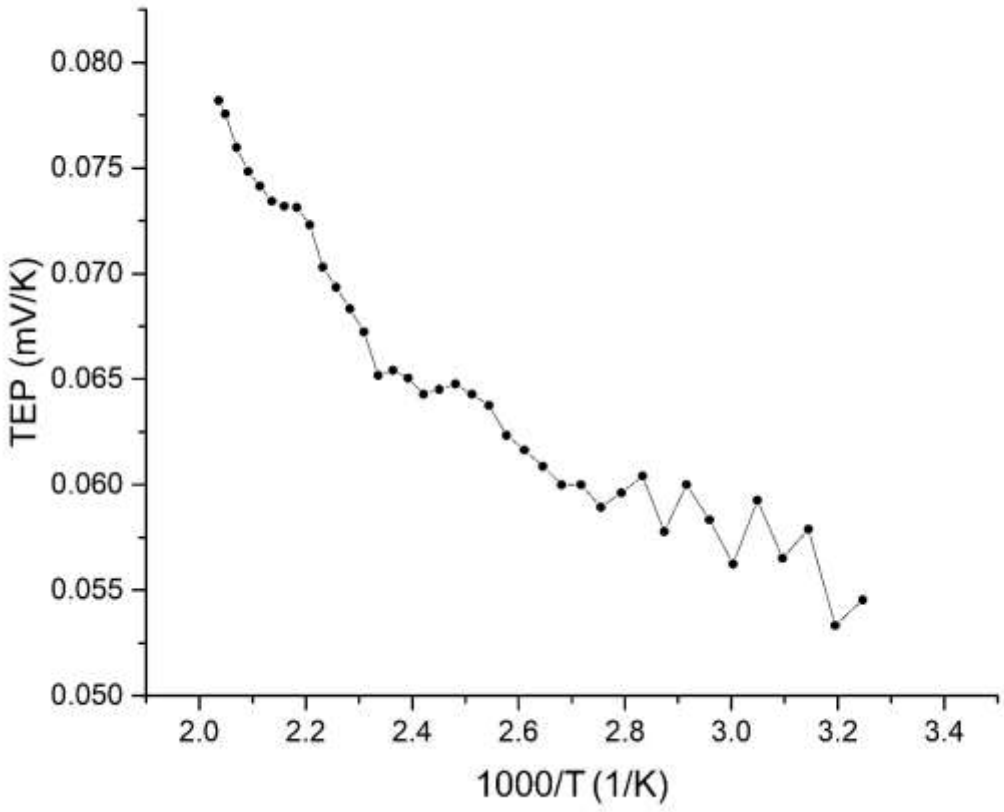

Figure - 14 Plot of the Thermoelectric power versus Inverse of Temperature for $InSb_{0.97}Bi_{0.03}$ crystal

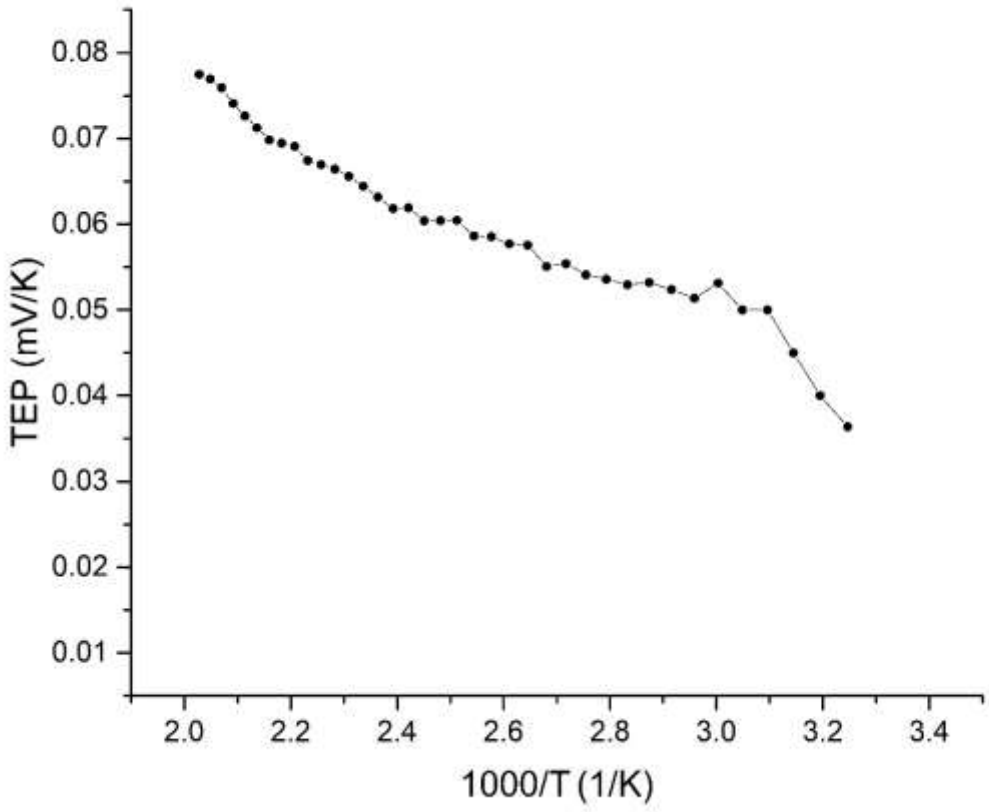

Figure - 15 Plot of the Thermoelectric power versus Inverse of Temperature for $InSb_{0.96}Bi_{0.04}$ crystal

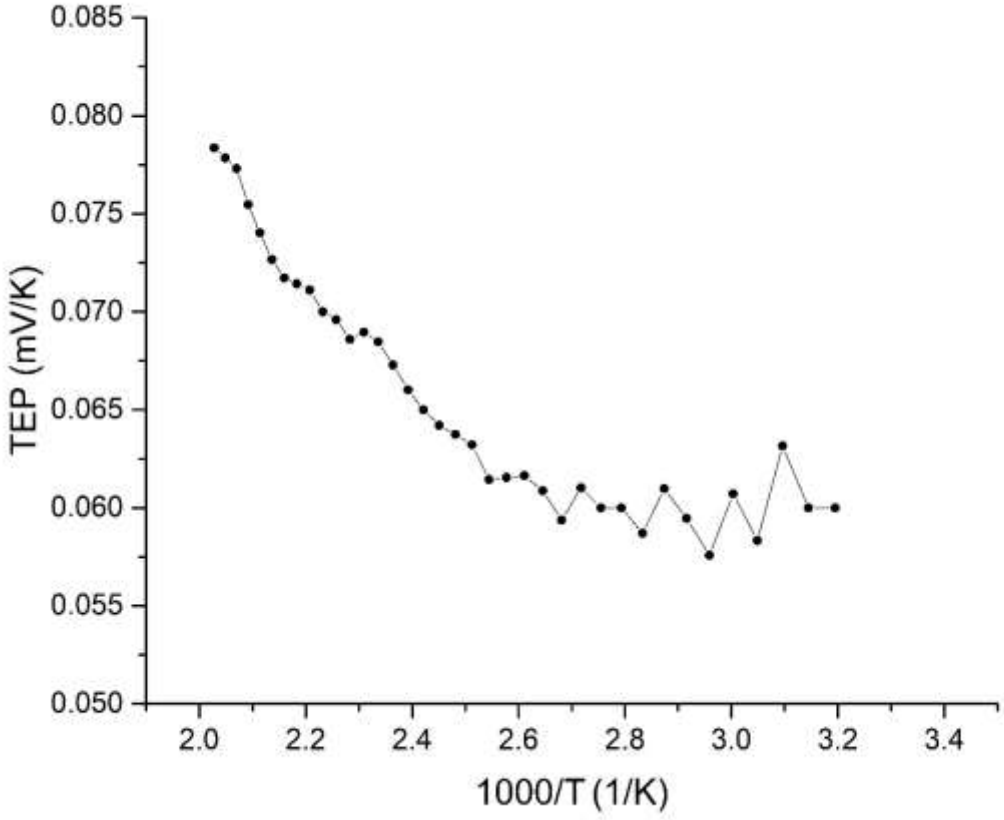

Figure - 16Plots of the Thermoelectric power versus Inverse of Temperaturefor $InSb_{0.95}Bi_{0.05}$ crystal

IV. Conclusions:

1. Large size and good quality crystals of $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) can be obtained with the use of the Bridgeman- Stockbarger technique.
2. From EDAX data and elemental mapping, the distribution of In, Sb, and Bi throughout the crystals was found uniform.
3. Sharpness of the XRD peaks obtained for $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals implies good crystallinity.
4. The observed and the JCPDS file values of structural data are found to be in fair agreement.From the JCPDS data one can conclude that $InSb_{1-x}Bi_x$ (x= 0.00, 0.03, 0.04, 0.05) crystals have a cubic structure with face centered lattice having space group $F\bar{4}3m$ (216).
5. The sign of Hall coefficient and thermal EMF show that all the crystals are of p-type, with carrier concentration of the order of 10^{18} cm^{-3}.
6. Hall co-efficient, carrier concentration and mobility of(i) InSb crystals were found to be2.5570 $\frac{cm^3}{coul}$, 21552 $\frac{cm^2}{V\,sec}$ and 2.4443cm^{-3}. (ii)$InSb_{0.97}Bi_{0.03}$ crystals were found to be 4.8948$\frac{cm^3}{coul}$, 11080$\frac{cm^2}{V\,sec}$and1.2769 cm^{-3}. (iii) $InSb_{0.96}Bi_{0.04}$ crystals were found to be 4.9201 $\frac{cm^3}{coul}$, 6275 $\frac{cm^2}{V\,sec}$and 1.2703 cm^{-3}. (iv) $InSb_{0.95}Bi_{0.05}$ crystals were found to be 2.5929$\frac{cm^3}{coul}$, 8405$\frac{cm^2}{V\,sec}$and2.4104 cm^{-3}.

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