CHAPTER 3

GROWTH AND CHARACTERIZATION OF DIRECTIONALLY SOLIDIFIED \( \text{InBi}_{1-x}\text{Sb}_x \) CRYSTALS
3.1 INTRODUCTION

A wide spectrum of technological applications is dependent on novel properties of crystals due to the nearly perfect three dimensional atomic arrangements. Monocrystals acquire unique features owing to crystallographic structure and absence of imperfections associated with grain boundaries. Recent advances in the field of communication, integrated circuits (IC), biomedical equipments, etc. have accelerated the demand. Narrow band gap III-V materials possessing favorable attributes have attracted the attention of researchers, as a special class of optoelectronic compounds. The non-availability of defect free samples prepared by conventional melt growth methods has been a concern in exploring their full potential. Therefore, in the present work, horizontal directional solidification (HDS) process was adopted to produce high quality crystals of pure and antimony doped indium bismuthide. This method allows crystallization of melt along a particular direction yielding nearly ideal crystals that could scientifically refine physical characteristics of the material. Substitution of a suitable dopant into InBi transforms the compound from semimetal to a semiconductor. Antimony can replace bismuth in the lattice, because they are iso-structural with same valency and nearly equal ionic size. Hence, the main objective of this research problem is to grow InBi$_{1-x}$Sb$_x$ ($x = 0-0.2$) crystals, not only having structural perfection but also of uniform chemical composition by optimizing the operational conditions and controlling growth environment. The results acquired from diverse analysis are discussed to explore their advantages for infrared (IR) detectors.
3.2 CRYSTAL GROWTH PROCESS

Semiconductors render adequate scope for scientific research, as it is possible to tailor their physical properties enabling device design with improved functionality. Therefore, enormous work has been done on developing materials in IR field, which are very significant for medical diagnostics, military and pollution control (Lee et al. 1997, Mohan et al. 2001). Owing to long carrier lifetime and spectral tunability, the II-VI family chalcogenides are useful for detectors (Rogalski et al. 2009, Lao et al. 2014). During the past few decades, this arena was dominated by mercury cadmium telluride (MCT) and other alloys. As MCT systems develop compositional, thermal, and lattice instabilities on account of the weak Hg-Te bond, narrow band gap III-V compounds are found to be more advantageous for IR technology (Chen et al. 1983). Though, numerous optoelectronic equipments utilize GaInSb samples, considerable work has not been progressed, due to poor crystallinity of the substrates grown from melts (Dutta 2005). Bismuth (Bi) containing semiconductors are fascinating, as the variation in Bi content changes their band gap (Rani, and Chadha 2002). Investigations were done on alloy systems such as InSb$_{1-x}$Bi$_x$, InSbBi, InSbAsBi, etc. by Wagener et al. (2000), Mohan et al. (2000) and Oszwaldowski et al. (2001). Since, InSb/InBi system is non-hazardous, it is suitable for IR optical devices at room temperature and incorporation of bismuth into InSb will change band gap in the range 0.172-1.5 eV (Jean and Hamon 1969, Lee and Razeghi 1998). According to Shah et al. (2010), doping will facilitate the conversion of InBi to a semiconductor, making it favorable for technological applications. InBi possesses tetragonal lattice with regard to basic unit cell (Binnie 1956) and hence, antimony as well as selenium could substitute bismuth in the lattice (Shah et al. 2010). Zone melting
and syringe pulling methods have been employed for the synthesis of InBi\textsubscript{1-x}Se\textsubscript{x} crystals (Shah et al. 2009, 2010). Dislocation density $\sim$10\textsuperscript{4} cm\textsuperscript{-2} was reported for the zone melted samples. Pandya et al. (1993) and Jani et al. (1994) studied impurity hardening in the melt grown tellurium doped InBi single crystals. Shah et al. (2007) noticed a softening effect in as-cleaved InBi\textsubscript{0.85}Sb\textsubscript{0.15} samples upon annealing. Khatri et al. (2009) have observed striations and lamellar growth features on InBiSb samples prepared by Bridgman technique. Measurements on single phase crystalline samples are essential for proper analysis of the inherent physical properties. Though, good quality crystals of large size have enormous importance in device fabrication, synthesis of bulk samples with perfect structure and less density of defects is a major challenge. Generally, supercooling will cause compositional variations and polycrystallinity in the crystals prepared by Bridgman, vertical gradient freeze and Czochralski methods (Dhanraj et al. 2010). Moreover, while using crystal wafers produced with the aid of these approaches for IC manufacturing, efficiency will be adversely affected by imperfections. In horizontal directional solidification (HDS) approach, such irregularities can be reduced by adjusting the growth parameters. Low defect density and high crystallinity are the benefits of HDS, since sample encounter lesser stress in comparison to other traditional melt processes (Dutta 2010). Therefore, this chapter unveils the investigations on growth and characterization of InBi\textsubscript{1-x}Sb\textsubscript{x} crystals by employing horizontal directional solidification.
**Compound charge synthesis and crystal growth**

An indispensable procedure for crystal growth is the synthesis of stoichiometric compound, for which high pure (99.999 \%) antimony, bismuth and indium purchased from Sigma-Aldrich, India, were used. The specially designed quartz tubes having length 10 cm and inner diameter 10 mm were cleaned by soap solution, dilute sulphuric acid, distilled water and acetone. Subsequently, ultrasonic cleaning utilizing double distilled water and hot air drying was performed. Ampoule containing elements in stoichiometric proportion was sealed under vacuum (10^{-6} mbar), placed in a muffle furnace (Fig. 3.1) and rotated at the speed of 60 rpm to ensure congruent melting of constituents during synthesis.

![Fig. 3.1: Sealed tube containing indium and bismuth elements.](image)

To avoid cracking of ampoule, temperature was slowly raised to 300 °C and 700 °C for growth of InBi and InBi_{1-x}Sb_x respectively. Based on the phase diagram reported by Okamoto (1991), weight percentage and synthesis temperature of InBi were chosen. Molten mixture was kept at steady temperature for nearly 12 h and the ampoule was gradually cooled to room temperature before harvesting the ingot (Fig. 3.2).
Identification and removal of impurities from the compounds is an essential requirement to obtain semiconducting crystals with appropriate stoichiometry. The polycrystalline ingot retrieved from the ampoule was subjected to compositional analysis using EDAX (Model: FUJITSU DX 2100). An integrated SEM-EDAX system equipped with detectors and computer software enabled a powerful analysis of weight percentage (wt.%). Fig. 3.3 depicts profile of stoichiometric InBi, which reveals absence of foreign elements other than the expected In and Bi.

The respective wt.% of In:Bi was found to be in concurrence with standard data (Table 3.1).
Table 3.1: Weight percentage of elements in the stoichiometric InBi charge.

<table>
<thead>
<tr>
<th>Element</th>
<th>Standard wt.%</th>
<th>Experimental wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>35.45</td>
<td>35.42</td>
</tr>
<tr>
<td>Bi</td>
<td>64.55</td>
<td>64.58</td>
</tr>
</tbody>
</table>

Systematic experimental trials have been delivered for the growth of stoichiometric, homogeneous InBi$_{1-x}$Sb$_x$ crystals through horizontal directional freezing approach. Initially, pre-cleaned ampoule filled with powdered compound charge sealed under a vacuum $10^{-3}$ mbar was placed in the furnace. Heater voltage was increased to attain a temperature of 300 °C and retained the same for 24 h. The system was cooled to room temperature for harvesting crystals. Fig. 3.4 illustrates the SEM image of grown sample, which discloses development of cracks and imperfections. EDAX analysis (Table 3.2) revealed non-stoichiometry due to significant oxygen diffusion. Thus, the probability of yielding homogenous crystals under low vacuum and fast cooling, has proven elusive. Therefore, subsequent runs were performed under high vacuum for longer growth periods, ensuring slow cooling.

Fig. 3.4: Cracks and defects on the surface of a non-stoichiometric crystal.
Table 3.2: Weight percentage of elements in the non-stoichiometric InBi crystal.

| Element | Standard (wt.% | Experimental (wt.% |  |
|---------|----------------|-------------------|
| In      | 35.45          | 30.26             |
| Bi      | 64.55          | 59.51             |
| O       | -              | 10.23             |

In addition to the application of scientific principles, growth of crystals is an art and one needs to be extremely careful in tackling the challenges involved in growth related complexities. For the growth trials, powdered charge was transferred into a quartz ampoule and sealed under a vacuum of $10^{-6}$ mbar. Microstructural defects like inclusions, voids, metallic precipitates, etc. will cause poor optical response of the obtained samples. Hence, for improving quality of crystals, growth runs were performed systematically, after calibrating the temperature profile of furnace. In order to eliminate the deleterious oxide content, a high vacuum ($10^{-6}$ mbar) pre-synthesis baking at 300 °C was conducted. For avoiding spurious nucleation near the tapered end, small inclination of about 10° was given for the loaded ampoule. Experiments were conducted by adjusting the temperature gradients of 4 °C /cm, 6 °C /cm and 8 °C /cm respectively, for a growth period of 48 h.

Traditional melt techniques have different intrinsic problems regarding the control of polycrystallinity and structural defects. However, HDS is an adaptable methodology for the synthesis of good quality crystals from melts at relatively low temperature, as it can effectively eliminate foreign particles (Nishi et al. 2010). Therefore, by
optimizing the operational conditions and temperature environment, special attention has been paid to grow crystals of InBi$_{1-x}$Sb$_x$ ($x = 0-0.2$) with uniform chemical composition. Mechanical polishing and subsequent rinsing in acetone as well as double distilled water were done for removing residual inclusions of particles which adhere to the surface during synthesis. Fig. 3.5 depicts the photograph of a grown InBi crystal, devoid of structural imperfections.

![Fig. 3.5: Harvested stoichiometric InBi crystal.](image1)

Wafers having thickness ~1 mm were sectioned from the grown crystals for investigating various characterization (Fig. 3.6).

![Fig. 3.6: Photograph of crystal wafers.](image2)
Microstructural analysis

Striations were observed on cleaved surfaces of those samples grown under the gradient of 4 °C/cm for a duration of 48 h (Fig. 3.7a), due to inhomogeneities induced during growth resulting from temperature fluctuations. Convective instabilities in heat flow caused structural irregularities, which are unfavorable for device applications.

Fig. 3.7a: SEM micrograph exhibiting striations.

Unsteadiness in synthesis environment leading to concentration variability along the growth direction has produced growth bands. According to Scheel and Fukuda (2003), thermal asymmetry and oscillations give rise to such modifications.

Fig. 3.7b: SEM micrograph exhibiting hillocks.
Fig. 3.7b depicts hillocks, as microstructural defects appeared on the grown samples, when temperature gradient was maintained at 8 °C/cm. As per the report of Muller et al. (2004), interface breaks up into dendrites, if melt is undercooled excessively and freezes rapidly resulting the solid to a meta-stable state. Upon increasing solid liquid interface temperature, instability occured in the solidification front and heat of crystallization was dissipated through melt leading to projections (Herlach 2015). These problems were not observed for the crystals grown under a temperature gradient, 6 °C/cm, which revealed smooth surface nearly free from micro cracks as evident in Fig. 3.7c

![Image](image.png)

Fig. 3.7c: SEM micrograph exhibiting smooth surface.

Under controlled growth environment, the restabilization of interface generates cellular regular pattern succeeded by even planar front. Therefore, in the present study, crystals grown under a temperature gradient, 6 °C/cm were selected for further investigations, as they were devoid of irregularities and imperfections.

Nanoscale imaging of material surfaces at high resolution using atomic force microscope (AFM) is inevitable for understanding various surface features. Three dimensional (3D) topographical image obtained in the non-contact mode of AFM (Model: NanoSurfAFM) is shown in Fig. 3.8.
Atomic force microscope coupled with detector computes surface roughness, peak-valley height, friction force, etc. To study the amplitude parameters, root mean square roughness ($R_{\text{rms}}$) was analysed and $R_{\text{rms}}$ value obtained for InBi sample is 0.515 nm. 3D AFM images with low roughness exhibited good crystalline structure. As a result of doping, $R_{\text{rms}}$ values were increased to 0.769 nm and 0.988 nm for InBi$_{0.9}$Sb$_{0.1}$ and InBi$_{0.8}$Sb$_{0.2}$ crystals respectively, because of structural modifications by impurity substitution.

3.3 COMPOSITION AND STRUCTURAL ANALYSIS

Special attention has been paid to explore homogeneity and structure of grown samples. In EDAX, the characteristic X-rays emitted from each constituent element was converted into an energy spectrum for evaluating chemical composition of materials over a scanning area. Figs. 3.9a,b represent profiles of crystals grown under a temperature gradient, 6 °C/cm.
Fig. 3.9a: EDAX profile of InBi crystal.

The weight percentage analysis of \( \text{InBi}_{1-x}\text{Sb}_x \) \( (x = 0-0.2) \) crystals is provided in Table 3.3, within an instrumental error of ± 2%.

Table 3.3: Weight percentage of elements in the grown \( \text{InBi}_{1-x}\text{Sb}_x \) crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard wt.%</th>
<th>Experimental wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
<td>Bi</td>
</tr>
<tr>
<td>\text{InBi}</td>
<td>35.45</td>
<td>64.55</td>
</tr>
<tr>
<td>\text{InBi}<em>{0.9}\text{Sb}</em>{0.1}</td>
<td>36.44</td>
<td>59.69</td>
</tr>
<tr>
<td>\text{InBi}<em>{0.8}\text{Sb}</em>{0.2}</td>
<td>37.47</td>
<td>54.58</td>
</tr>
</tbody>
</table>

Computed wt.% of elements are found to be in agreement with the standard values, which is due to optimization of growth conditions employed for directional solidification process.
Fig. 3.9b: EDAX profile of InBi$_{0.9}$Sb$_{0.1}$ crystal.

Generally, when the radii of host and dopant atoms differ by not more than 15 %, a substitutional solid solution is feasible (Rani and Chadha 2002). It is deduced from compositional study that, effective incorporation of antimony in InBi lattice has taken place, as the radius of antimony and bismuth atoms varies only by 10.34 %.

Powder X-ray diffraction (PXRD) has become an indispensable method for structural characterization and quality control of materials. It is a non-destructive technique for analyzing a wide range of specimens such as plastics, metals, minerals, semiconductors and ceramics. Since phase identification and evaluation of lattice parameters are inevitable to assess the perfection of grown crystals, XRD data were recorded (Model: X’ pert diffractometer) using CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å); with a scan step of 0.03 °/s. The diffractograms exhibited sharp peaks (Fig. 3.10) indicating fairly ordered structure, good crystallinity and absence of polymorphism. Evaluated lattice constants (Table 3.4), match well with the reported values of Binnie (1956) and White et al. (1975).
Fig. 3.10: X-ray diffractograms of InBi$_{1-x}$Sb$_x$ crystals.

Moreover, characteristics of well defined peaks observed for crystals grown corresponding to 6 °C/cm matches well with standard structure, reflecting the size and shape of unit cell. Such features were not evident in the crystals synthesized for 4 °C/cm and 8 °C/cm, since they possess striations and inhomogeneities. For InB$_{0.9}$Sb$_{0.1}$ and InB$_{0.8}$Sb$_{0.2}$ crystals, a marginal decrease in intensity was observed, as presence of impurities decreases the amplitude of diffracted beam. According to Cullity (2001), Tanner and Bowen (2006), the strain fields around substitutional atoms can regionally cause deformation in the lattice, violating Bragg’s condition, $2dsin\theta = n\lambda$, which inturn diminishes intensity of diffracted
beam. Interplanar spacing, $d$ and lattice constants, $a$ and $c$ are related by the equation,

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (3.1)$$

Table 3.4: Lattice parameters of the grown $\text{InBi}_{1-x}\text{Sb}_x$ crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a = b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{InBi}$</td>
<td>4.9894</td>
<td>4.7835</td>
</tr>
<tr>
<td>$\text{InBi}<em>{0.9}\text{Sb}</em>{0.1}$</td>
<td>4.9890</td>
<td>4.7830</td>
</tr>
<tr>
<td>$\text{InBi}<em>{0.8}\text{Sb}</em>{0.2}$</td>
<td>4.9879</td>
<td>4.7815</td>
</tr>
</tbody>
</table>

Decrease in lattice parameters (Table 3.4) of $\text{InBi}_{0.9}\text{Sb}_{0.1}$ and $\text{InBi}_{0.8}\text{Sb}_{0.2}$ can be correlated to incorporation of $\text{Sb}$ atoms having smaller radii ($r_{\text{Sb}} = 0.145$ nm) than $\text{Bi}$ ($r_{\text{Bi}} = 0.160$ nm). Thus, the results verified that, substitutional antimony doping has materialised to improve the semiconducting property of crystals grown by the HDS process.

### 3.4 RAMAN SPECTROSCOPIC STUDIES

Raman spectroscopy investigates molecular and crystal lattice vibrations to obtain information about chemical environment, composition, defect density, bonding and structure of the material. Non-periodicity of atoms causes lower efficiency and therefore, data about the crystallinity are essential for device fabrication. Structural quality of indium antimonide crystals evaluated by Raman spectroscopy, revealed an intense sharp peak at 178 cm$^{-1}$ (Gadkari 2012). With the help of this analysis, Udayasankar and Bhat (2003) have established the correlation between surface morphology and crystallinity. Considering the importance of Raman spectroscopic tool, studies have been performed on $\text{InBi}_{1-x}\text{Sb}_x$ crystals for supporting XRD analysis with regard to
homogeneity and quality. Microscope equipped with 532 nm laser as an excitation source (Model: Witech focus innovations alpha 300 R) was employed for recording the spectra at room temperature. Fig. 3.11 displays the Raman spectra of pure and Sb doped InBi samples exhibiting distinct intense narrow peaks, indicating uniform bond strength.

![Raman spectra of pure and doped samples.](image)

Fig. 3.11: Raman spectra of pure and doped samples.

Wide diffused spectral features were not observed, manifesting the absence of damages and defects in the lattice. Doped samples revealed a small peak shift towards higher frequency in Raman spectroscopic profiles. These variations can be correlated to changes in bond length and energy levels due to difference in mass as well as radii of bismuth and antimony.
3.5 THERMAL MEASUREMENTS

Direct crystallization so as to form a desired structure is essential for obtaining the unique characteristics of materials. For establishing well defined relation between temperature and specific thermal properties of substances, differential scanning calorimetry (DSC) is the best suited scientific process. It measures enthalpy changes during phase transitions such as solidification, vaporization and re-crystallization. To confirm the melting point (M.P) and presence of sub states, InBi$_{1-x}$Sb$_x$ crystals were subjected to DSC under different heating/cooling cycles. Calorimetric studies were performed on powders of pure and doped samples in sealed aluminium pans, employing Mettler Toledo analyzer. DSC measurements in a scanning temperature range 25-300 °C, with heating rate of 10 °C per minute are recorded as shown in Fig. 3.12.

![DSC plot of InBi crystal](image)

**Fig. 3.12: DSC plot of InBi crystal.**

It is evident from the DSC plot that, crystals melted within a narrow range, exhibiting an intense endothermic peak. Low temperature region of the peak is fairly straight, indicating single phase, chemical
homogeneity and purity of crystals. The estimated melting point of InBi, InBi$_{0.9}$Sb$_{0.1}$ and InBi$_{0.8}$Sb$_{0.2}$ samples are 109.43, 121.13 and 136.21 °C respectively. Upon Sb substitution, the melting point was enhanced due to modifications in chemical bonding. Electronegativity and size difference between the incorporated (antimony) and host (bismuth) atoms have created local strains resulting changes in bond energy, as explained by Dhanraj et al. (2010). Addition of Sb in Bi leads to an increase in ionic bonding and melting point, caused by higher electronegativity of antimony than bismuth according to Pauling scale.

Phase diagram unravels informations rich enough for material, enabling the suitability of crystals for technological applications. Based on the phase transformation as shown in Fig. 3.13, the grown crystals were analyzed. In accordance with the findings of Okamoto (1991), InBi samples exhibited single phase. Thus, the plot discloses composition limits and temperature, within which, different components of InBi compound are found to be stable. Melting point data recorded from DSC studies proved the absence of In$_2$Bi and In$_3$Bi, as reported by Cruceanu et al. (1975), whereas it conforms well to that of pure InBi (M.P = 109.43 °C), indicating its stoichiometry. Furthermore, the results obtained agree with EDAX analysis and revealed that, the estimated atomic percent of indium and bismuth matches as per the phase diagram.
3.6 ELECTRICAL CHARACTERIZATION

The concentration of doped impurities critically affects performance and reliability of optoelectronic devices. For obtaining information about the transport properties of grown samples, Hall effect studies were done at 300 K, by applying a magnetic field (±5 K Gauss) and current (±10 mA). Resistivity measurements were carried out in the temperature range, 300-380 K, using four probe set up (Model DFP-02). Hall coefficient remains negative, indicating \( n \)-type conductivity for the doped crystals. The estimated free carrier concentration for \( \text{InBi}_{1-x}\text{Sb}_x \) (\( x = 0.1, 0.2 \)) are \( 7.8 \times 10^{16} \) and \( 4.6 \times 10^{16} \) cm\(^{-3} \) respectively, whereas the corresponding values of mobility are 37419 and 26222 cm\(^2\)/Vs. Samples revealed a decrease in resistivity with temperature (Fig. 3.14), manifesting the characteristic property of semiconductors.
Electrons that can move freely are responsible for electrical conductivity ($\sigma$) in the presence of an external electric field. Thermal energy excites a fraction of valence electrons into conduction band. With rise in temperature, population of charge carriers to higher energy levels enhances, thereby reducing electrical resistivity. Temperature dependence of $\rho$ is given by the expression,

$$\rho = A e^{\frac{E_g}{2kT}}$$  \hspace{1cm} (3.2)

where, $E_g$ is band gap, $T$ is temperature, $k$ is Boltzmann constant and $A$ is a constant. Plot of $\log \rho$ against $1/T$ shows a linear relation and from the slope ($S$), $E_g$ was estimated based on the formula,

$$E_g = 2.3026 \times 10^3 \times 2k \times S$$  \hspace{1cm} (3.3)

Electrical behavior of InBi$_{0.9}$Sb$_{0.1}$ and InBi$_{0.8}$Sb$_{0.2}$ samples reflected the semiconducting nature, showing the typical band gap values, 0.178 and
0.183 eV respectively. The semimetallic nature of indium bismuthide is on account of the inverted band structure, where valence band maximum lie higher than the conduction band minimum. Incorporation of Sb develops strong interaction between the bands, which results a shift in Fermi level, leading to energy gap variation. Shah et al. (2010) have reported a semimetal-semiconductor transition in selenium doped InBi crystals. Thus, substitution of antimony in InBi lattice transformed indium bismuthide into a narrow band gap compound.

3.7 MICROHARDNESS STUDIES

Hardness of a material is referred as the resistance offered to local deformation and is an important mechanical property. Defects, impurities, dislocations and crystal structure are key factors, which govern the strength of a material. Therefore, microhardness of the as-grown crystals was determined using Vickers hardness tester (Model: MVH-I). This is a non-invasive testing tool, since the specimen surface will not be damaged significantly due to indentations (Renjo et al. 2014). Prior to measurements, the instrument was calibrated and several data were recorded for loads in the range 5-100 g with a dwell time of 10 seconds. To prevent interactions of neighboring indentations, care was taken to set distance more than two times the length of diagonal impression. Vickers hardness ($H_v$) was computed as per the formula,

$$H_v = \frac{1.854P}{d^2}$$

where, $P$ is applied load and $d$ is average value of the diagonal length. It was observed that, $H_v$ increases with load (Fig. 3.15), as the lattice offers resistance to dislocations created locally, as per the findings of Kunjomana and Mathai (1992).
The overall variation of $H_v$ with load depends on growth mechanism and intrinsic defects in the material. In addition, for covalent compounds, the strength of chemical bonds and periodic atomic distribution dominate hardness. With the increase of applied load, $H_v$ is found to enhance and attains limiting value beyond a threshold load of 35 g, owing to intensive saturation of the covalent bonds. When dopants are incorporated, interactions between the defects restrict movement of dislocations created by indentation. Addition of an atom, which is smaller than the host, produces tensile strain to lattice and hence a larger stress is needed to initiate deformation (Callister 2007). Thus, strengthening effect due to substitution of $Sb$, caused an increase in $H_v$, and attained saturation at higher loads. The grown InBi$_{1-x}$Sb$_x$ crystals by HDS technique are found to be stronger and stable than the zone melted crystals (Shah et al. 2007).

Load dependence of $H_v$ can further be illustrated, based on Meyer’s law for a pyramidal indenter in the form,
\( P = ad^n \) \hspace{1cm} (3.5)

where, \( P \) is applied load, \( a \) is material constant, \( d \) is average diagonal length of impressions and \( n \) is work hardening coefficient. From equation (3.5),

\[
\log P = \log a + n \log d \hspace{1cm} (3.6)
\]

Slope of the linear plot between \( \log P \) and \( \log d \) gives the value \( n \), which indicates indentation size effect (ISE). By combining equations (3.4) and (3.5),

\[
H_v = bd^{n-2} \hspace{1cm} (3.7)
\]

where, \( b \) is a constant. If \( n < 2 \), normal ISE occurs, which reflects decrease in \( H_v \) with applied load and \( n > 2 \) implies reverse ISE. According to Onitsch (1950), the latter indicates increased hardness and strength of material.
Fig. 3.16: Meyer’s plot of InBi$_{1-x}$Sb$_x$ crystals.

By linear regression analysis of the graph (Fig. 3.16), the estimated values of work hardening index $n$ are 2.02, 2.11 and 2.08 for InBi, InBi$_{0.9}$Sb$_{0.1}$ and InBi$_{0.8}$Sb$_{0.2}$ respectively. Thus, improvement in mechanical properties as well as quality of crystals manifested the right choice of growth method, controlled environment and doping.

3.8 FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDIES

For probing band structure of a material, the most direct method is to analyze its optical transmission spectrum. By observing functional dependence of intensity and wavelength, one can investigate the distribution of permitted energy levels as well as possible electron transitions. Studies on optical transition and band gap are feasible with Fourier transform infrared (FTIR) spectroscopic response of sample. Room temperature IR transmittance spectra of InBi$_{1-x}$Sb$_x$ crystals recorded using FTIR spectrometer (Model: Thermo-Nicolet 200) in the 400-4000 cm$^{-1}$ range are presented (Fig. 3.17).
Fig. 3.17: Transmission spectra of InBi$_{1-x}$Sb$_x$ crystals.

Fairly good optical transmission, devoid of significant scattering, has been exhibited by samples, indicating good quality and homogeneity. The value of band gap ($E_g$) was computed, utilizing Wood and Tauc (1972) expression,

$$\alpha(h\nu) = B(h\nu - E_g)^n$$  \hspace{1cm} (3.8)

where, $\alpha$ is absorption coefficient, $B$ is a constant, $h\nu$ is incident energy, and $n$ is fitting exponent ($n = 1/2$ and 2 for direct and indirect transitions). $E_g$ was estimated from photon energy ($h\nu$) versus $(ah\nu)^2$ plot (Fig. 3.18). The evaluated values of $E_g$ for InBi$_{0.9}$Sb$_{0.1}$ and InBi$_{0.8}$Sb$_{0.2}$ samples are 0.165 and 0.173 eV respectively.
Fig. 3.18: Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ for InBi$_{1-x}$Sb$_x$ crystals.

The band gaps determined from electrical and optical characterization are presented in Table 3.5. The variation in $E_g$ can be attributed to the introduction of energy levels in valence and conduction bands as a result of antimony incorporation (Dey et al.2002). Thus, increase in band gap with doping enhances the semiconducting property.
Table 3.5: Energy gap of the grown InBi$_{1-x}$Sb$_x$ crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity measurement $E_g$ (eV)</th>
<th>Transmittance measurement $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InBi$<em>{0.9}$Sb$</em>{0.1}$</td>
<td>0.178</td>
<td>0.165</td>
</tr>
<tr>
<td>InBi$<em>{0.8}$Sb$</em>{0.2}$</td>
<td>0.183</td>
<td>0.173</td>
</tr>
</tbody>
</table>

The values of $E_g$ determined from optical transmission studies is found to be less compared to carrier transport measurements (Table 3.5), owing to strong electron-hole interaction and the exciton binding energy, as proposed by Sariciftci (1997). Thus, optimized antimony doping could bring significant changes in the value of energy gap, favorable for IR applications.

### 3.9 DIELECTRIC MEASUREMENTS

Evaluation of parameters such as permittivity, dielectric loss, impedance, etc. is inevitable to gain valuable information about a sample, for careful design of electronic devices. Hence, capacitance of the grown crystals was measured over a specific frequency (100-1MHz) and temperature (300-400 K) range, employing an impedance analyzer (Model: AGILENT 4284A) within an accuracy of ± 2 %. Investigations on pure InBi were carried out in the temperature range, 308-353K, due to its low melting point. Dielectric constant ($\varepsilon$) was computed with the formula,

$$\varepsilon = \frac{Ct}{\varepsilon_0 A}$$ (3.9)
where, $C$ is capacitance, $t$ is thickness, $A$ is cross-sectional area of the sample and $\varepsilon_0$ is permittivity of free space. The dependence of dielectric constant on temperature and frequency for the grown InBi$_{1-x}$Sb$_x$ samples are shown in Fig. 3.19a-c.

Fig. 3.19a: Dielectric constant versus temperature for InBi crystal.

Fig. 3.19b: Dielectric constant versus temperature for InBi$_{0.9}$Sb$_{0.1}$ crystal.
Dielectric constant decreases with frequency, which can be interpreted based on the contribution of electronic, ionic, orientational and interfacial polarizability. With increase in frequency, orientation of dipoles slows down and lags behind the field, thereby decreasing $\varepsilon$. Rise in temperature facilitates the alignment of dipoles and interfacial polarization. Dielectric constant is found to enhance with percentage of antimony, as it contributes ionic polarization. Charges on the substitutional defects can be quickly redistributed at low frequency, leading to an increase in dielectric constant (Fischetti and Vandenberghe 2016).

It is well known that, dielectric loss ($\tan \delta$) is the dissipation of energy due to movement of charges in an electromagnetic field, when polarization switches direction. Materials exhibit two types of energy losses, owing to charge flow and dipole rotation in an alternating electric (AC) field. When a sample is subjected to varying electric field, absorption of energy will result in dielectric loss. It is a measure of the
degree to which a dipole is out of phase with applied electric field. Its low value ensures minimum power loss in the material. The variation of $\tan \delta$ with temperature is depicted in Figs. 3.20a-c.

![Graph showing dielectric loss versus temperature for InBi crystal.](image)

**Fig. 3.20a:** Dielectric loss versus temperature for InBi crystal.

![Graph showing dielectric loss versus temperature for InBi$_{0.9}$Sb$_{0.1}$ crystal.](image)

**Fig. 3.20b:** Dielectric loss versus temperature for InBi$_{0.9}$Sb$_{0.1}$ crystal.
Variation of dielectric loss with temperature is ascribed to the random movement of dipoles. Decrease in $\tan \delta$ with frequency can be correlated to the pinning of domain walls on randomly distributed defects. The swift periodic change of field in high frequency region decreases such effects, thereby reducing these parameters (Damjanovic 1998).

3.10 CONCLUSIONS

Stoichiometric InBi$_{1-x}$Sb$_x$ ($x = 0-0.2$) crystals were grown by employing horizontal directional solidification (HDS) method in a well controlled growth environment comprising precise temperature controllers and relay mechanism. Influence of antimony doping and growth parameters on the structural, mechanical, optical and electrical properties has been explored for the first time. Different trials (temperature gradient 4 °C/cm, 6 °C/cm and 8 °C/cm) were executed for growth under a duration of 48 h, wherein the typical condition governed by 6 °C/cm was found to be ideal for synthesis of good quality
homogeneous crystals with optically smooth surface. Higher temperature gradient and growth period led to surface irregularities resulting from thermal shock. With the help of EDAX profiles, antimony incorporation in indium bismuthide was confirmed. Good crystalline nature and structure were revealed by XRD, Raman and DSC analysis. The melting points of InBi, InBi$_{0.9}$Sb$_{0.1}$ and InBi$_{0.8}$Sb$_{0.2}$ samples were found to be 109.43 °C, 121.13 °C and 136.21 °C respectively. Vickers microhardness was enhanced and saturated at higher loads, due to the presence of covalent bonds coupled with stability of grown surface. Meyer’s index, $n$ was greater than 2, implying the strength of samples as per reverse indentation size effect. HDS grown InBi$_{0.9}$ Sb$_{0.1}$ and InBi$_{0.8}$Sb$_{0.2}$ samples provided desirable optical band gap of 0.165 and 0.173 eV respectively. Upon doping InBi with Sb, semimetallic to semiconducting transition was accomplished. Thus, proper control of doping and growth parameters could enable the directionally solidified crystals to achieve characteristics favorable for infrared device applications.