PART – II

CHAPTER – 6

GROWTH OF $InBi_{1-x}Sb_x$ AND $InBi_{1-x}Se_x$ SINGLE CRYSTALS

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The III - V intermetallic compound InBi is an equilibrium phase in the In-Bi alloy system, occurring at 50 at.% each. It has a low melting point (109.5 ^{0}C) (Giessen et al)[1] and also, crystallizes into a tetragonal non-polar structure unlike the other III - V compounds (Chung et al)[2] which usually crystallize into the cubic polar structures. Because of its low melting point and easy cleavage makes it attractive for basic studies and also, it can easily attain a thermal equilibrium reducing the degree of super cooling during crystal growth from melt. However the crystal is quite soft (Bhatt et al)[3] and its resistivity has been reported to be of the order of 10^{-4} ohm-cm (Krivov et al)[4]

InBi single crystals have been grown by various methods like Bridgman, Czochralski, Zone melting by various workers (Asanabe, Bhatt et al, Fischler, Roy et al, Saito, Thorsen et al, Shapira et al and Walter[5,3,6-11]).Whisker growth of InBi crystal has been reported by Huckle et al[12], using " Squeeze technique".

The ternary system In-Sb-Bi has been a candidate for band gap tuning for quite a time. In efforts to obtain crystals of band gap less than that of InSb (Eg = 0.16 eV) there have been reports of crystal growth of $InSb_{1-x}Bi_x$ with varying x and of structure modification of InSb.

Kumagawa et al[13] have successfully grown $InSb_{1-x}Bi_x$($x < 0.03$) by normal Bridgman method, whereas Ozawa et al[14] have used high speed rotation technique to grow these crystals by the Bridgman method. These workers have observed the Bi composition ratio to vary along the growth direction. Desai and Naik[15] have used the zone melting method to grow these crystals with $x \leq 0.05$ and found indications of structure modification. However the crystal perfection obtained by these workers has been very poor.

Choice of InBi as the base material is an alternative approach to obtain a semiconductor by addition of suitable third component. This is because the InBi crystals can be grown with quite high perfection without any elaborate growth conditions and equipment (Bhatt et al and G.R Pandya et al)[16, 17].

Jani et al have grown Te-doped InBi single crystals by Zone melting[18] and Syringe pulling[19] methods. However, there is no report of crystal growth of InBi doped with Sb or Se as an impurity. The present work therefore concerns $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$. The study is mainly concentrated on the zone melting method. The syringe pulling method has also been used and results are reported. In the present work, a predetermined quantity of Antimony/Selenium was added to InBi compound with an aim to study its effect on crystal growth, crystal perfection, hardness and also optical as well as electrical nature of InBi.

Indium, Bismuth, Antimony and Selenium each of 99.999 % purity (5 N purity) were purchased from Nuclear Fuel Complex, Hyderabad, India. The stoichiometric amounts of all the materials were weighed accurately up to 10 micrograms using a semi-microbalance and filled in a quartz ampoule of about 10 cm length and 1 cm diameter. The quartz tube was then vacuum-sealed at a pressure of about 10^{-4} Pa and it was kept in the alloy-mixing furnace (chapter-5). In this mixing unit, the material was mixed in the molten state for about 48 hours by rotating the tube at 10 rpm at 730 ^{0}C temperature. The rotation of the tube was stopped and the material was further kept in the molten state for further 24 hours in order to ensure homogenization and complete reaction in the molten charge. It was then slowly cooled to room temperature. This process usually produces fairly homogeneous compound. The ingot so prepared was subjected to growth by zone melting.

The $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ (where x = 0.2, 0.3, 0.4) compounds prepared as discussed above were used for growing single crystals by zone melting method. The starting ingot was about 6 cm in length and 0.8 to 1 cm in diameter. The temperature profile of the zone – furnace is shown in Fig. 1. First the ingot was zone leveled. The temperature gradient across the two solid – liquid interfaces was obtained to be about 30 ^{0}C / cm by controlling the furnace temperature within $\pm$ 1 ^{0}C, giving a zone length of about 8 to 10 mm. The maximum zone

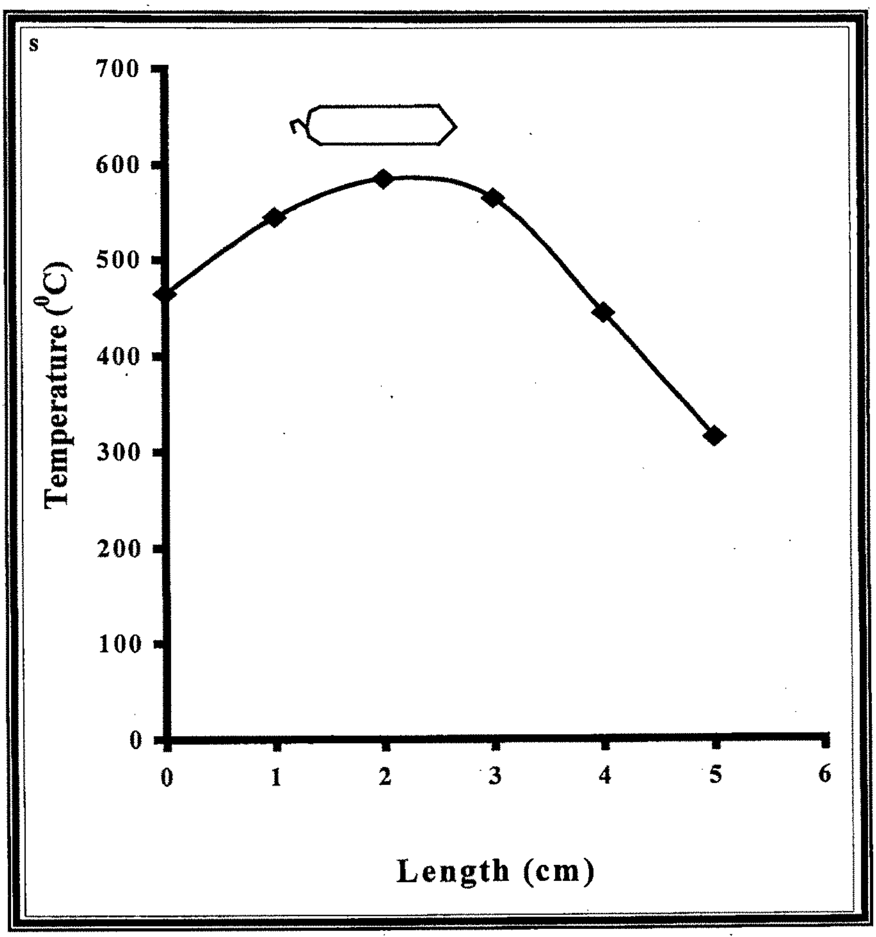

s
700
600
500
400
300
200
100
0
Temperature (^{0}C)
0
1
2
3
4
5
6
Length (cm)

Fig. 1

temperature was ~50 ^0C above the melting point. To level off impurities, 8 passes in alternate directions were given and finally the last pass was used to obtain self-nucleated single crystals. To obtain good quality crystals, it was found necessary to give sufficient time to the first molten zone before starting the zone travel to achieve stable conditions. The growth velocity was 1 cm / hr. Crystals with x up to 0.5 were grown at the same growth velocity and temperature gradient. The quality of the crystals obtained was judged by examining the cleavage surfaces and also by dislocation density measurements using the etching technique (Chapter-7). The XRD characterization of the crystals was also carried out. The diffractometer used is described in Chapter-5.

The X – ray diffractogram of powdered samples from the crystals exhibited peaks corresponding to InBi, InSb and Sb and InBi, InSe and Se. The diffractograms obtained for $InBi_{0.8}Sb_{0.2}$ and $InBi_{0.8}Se_{0.2}$ single crystals, respectively, are shown in Fig.2 and Fig.3. The peak indexing is also shown in the figures.

$InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ (where x = 0.2, 0.3, 0.4) crystals grown were cleaved on ice to minimize deformation due to cleavage process. The cleavage plane (001) was observed to be quite plane and mirror like, nearly as in the case of InBi crystals.

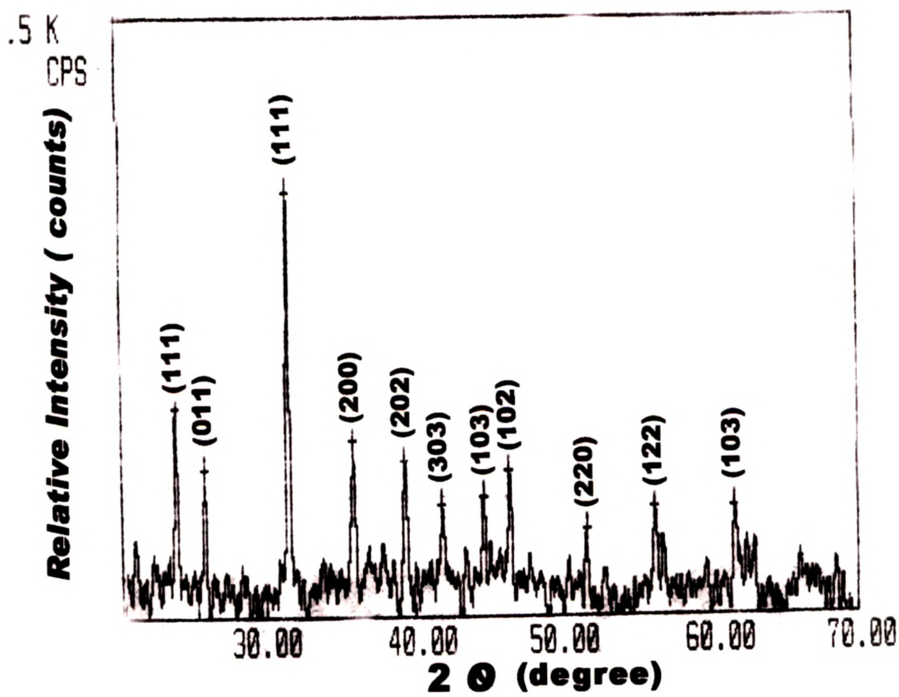

.5 K
CPS
Relative Intensity (counts)
(111)
(111)
(011)
(200)
(202)
(303)
(103)
(102)
(220)
(122)
(103)
30.00
40.00
50.00
60.00
70.00
2 Θ (degree)

Fig. 2

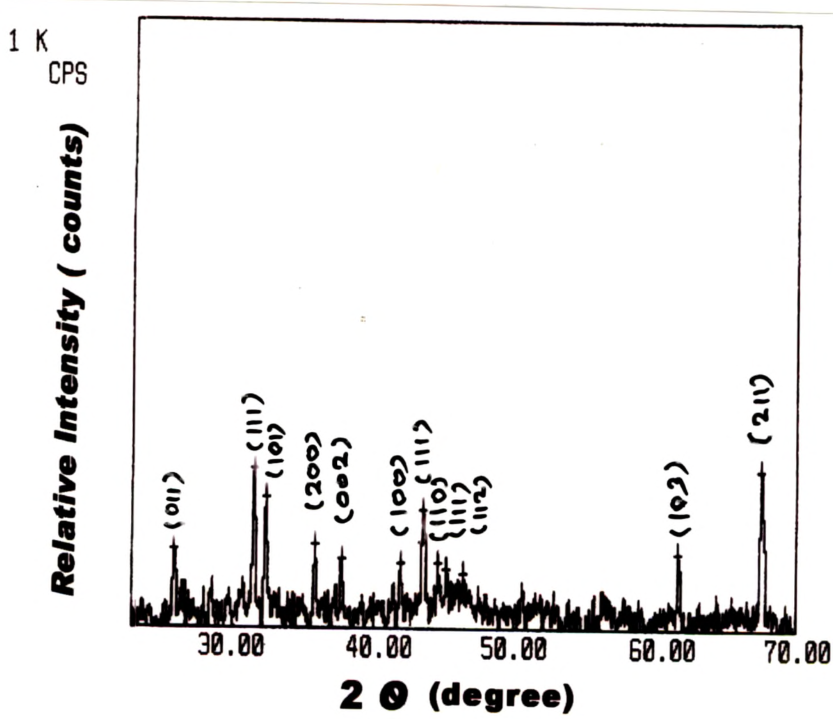

1 K
CPS
Relative Intensity (counts)
(011)
(111)
(101)
(200)
(002)
(100)
(111)
(110)
(111)
(112)
(102)
(211)
30.00
40.00
50.00
60.00
70.00
2 Θ (degree)

Fig. 3

EFFECT OF IMPURITY CONCENTRATION ON CRYSTAL PERFECTION :

To study this the effect the growth velocity was kept constant at 1 cm/hr and crystals were grown with different impurity concentrations. For quantitative assessment of perfection the methods of etch-pit count on the cleavage plane was used for determining dislocation densities. On each etched sample-surface, a minimum of 5 to 6 regions were scanned and the averages were obtained. The dislocation density was measured on samples obtained from three widely separated portions of each crystal ingot. Table-1 represents the average results of dependence of crystal perfection on Sb and Se concentration. The results indicate that the dislocation density increases with concentration of impurity.

This fact is also reflected in the nature of cleavage of the crystals. Fig.4(a) and (b) and Fig.5(a) and (b) show the photographs of the cleavage counter surfaces of $InBi_{0.8}Sb_{0.2}$ and $InBi_{0.6}Sb_{0.4}$ crystals. It is observed that there is good one to one correspondence of surface patterns. Also the apparent perfection as appears from the number of cleavage lines and their step sizes is better at lower impurity concentration than at the higher.

Table-1

IMPURITY (X)	DISLOCATION DENSITY (cm^{-2}) IN	
	$InBi_{1-x}Sb_x$	$InBi_{1-x}Se_x$
0.2	2×10^4	2.5×10^4
0.3	3×10^4	3.5×10^4
0.4	4.5×10^4	5.0×10^4

Fig. 4(a) **X 100** **Fig. 4(b)** **X 100**

Fig. 5(a) X 100

Fig. 5(b) X 100

EFFECT OF NUMBER OF ZONE PASSES ON CRYSTAL PERFECTION :

It is known that while using the zone melting method of crystal growth, the technique of zone leveling is very effective in uniform distribution of impurity. As a result of the uniform impurity distribution, the zone leveling also improves the crystal perfection. This is because the differences in impurity concentration along the crystal can produce fairly large number of dislocations. This effect may be to an extent that a continuous change in the solute content can nucleate a lineage structure as speculated by Frank[20]. A sufficient experimental evidence in this respect has been reported as long back as 1956 (Goss et al and Pfann[21-22]. Thus, since number of zone passes affects homogeneity and hence the perfection of crystals, at least four crystals were grown with large number of alternate zone leveling passes, namely 30. For these growths the growth velocity and the Sb/Se content were kept constant at 1cm/hr, x = 0.2, respectively. The crystal perfection was assessed by process identical to that used for crystals grown with eight zone-levelling passes. The dislocation density was measured on a number of samples from three different regions of the crystal ingot. It was observed that there was no significant variation of dislocation density across a given ingot as well as across a given cleavage surface. The values were averaged over all samples of crystals of individual compositions. The results are shown in

Table-2. Evidently the perfection shows quite a significant improvement by increasing the number of zone levelling passes. Remarkably, this feature has also been found to bear a dramatic effect on the applied load dependence of indentation hardness (to be discussed in Chapter-8).

GROWTH FEATURES ON AS GROWN $InBi_{1-x}Sb_x$ CRYSTALS :

On the top free surface of as grown $InBi_{1-x}Sb_x$ crystals, some interesting growth features were observed under optical microscope. These are described below.

The free surface of the as grown crystal was frequently observed to have triangular terraced features. A typical observation obtained on the as grown surface of $InBi_{0.8}Sb_{0.2}$ crystal grown with 8 zone levelling passes is shown in Figure-6. These triangles are also of the same orientation as in Figure-7, which shows a number of such features at lower magnification. Also, the triangles are nearly equilateral. The crystal structure being approximately that of cubic type (c/a = 0.95) these features imply the observation surface to be of (111) orientation. Hence, planes of {111} type may be responsible to develop growth fronts resulting in these features.

In melt grown crystals, striations are not unusual particularly in the cases of alloys. In the present case the striations were observed on the

Table – 2

Variation of dislocation density with number of zone passes for x = 0.2 of the indicated impurity

No. OF ALTERNATE ZONE PASSES	DISLOCATION DENSITY (cm^{-2}) IN	
	Sb	Se
8	2.0×10^4	2.5×10^4
30	1.0×10^4	1.5×10^4

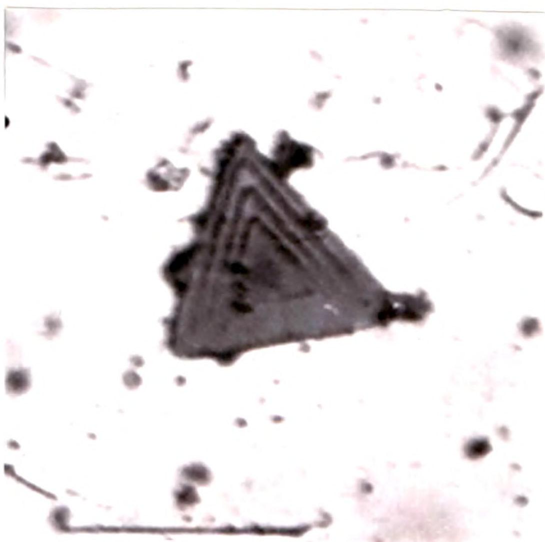


Fig. 6 X 400

Fig. 7 X 200

as grown free surfaces of almost all crystals. However, it is noteworthy that their appearance is more conspicuous in the case of crystals grown with 30 zone levelling passes. A typical example is shown in figure-8. These are striations on the top free surface of as grown $InBi_{0.8}Sb_{0.2}$ crystals. These striations were observed to be perpendicular to the crystal ingot axis. They are parallel and nearly equally spaced indicating crystallographic associations. In this regard it is possible that some crystallographic plane like {111} may be responsible for these features. This is because the layer growth mechanism has been reported to give rise to such striations (Desai et al)[(23)].

GROWTH FEATURES ON $InBi_{1-x}$ Se_x CRYSTALS:

In the case of $InBi_{1-x}Se_x$ crystals it should be noted that selenium has quite a higher vapour pressure than that of the rest of the elements. The features observed on these crystals therefore exhibited significant contrast compared to those observed in the case of $InBi_{1-x}Se_x$ crystal. Fig.9 illustrates an example. This is a photograph of features on $InBi_{0.8}Se_{0.2}$ crystal grown with 8 zone levelling passes. The rectangular facets observed have random orientations. These may be due to condensation of Se vapours on the top free surface of the crystal. Fig.10 shows features observed on another crystal but of different type. The concentric circular structures with dark centers are observed to have

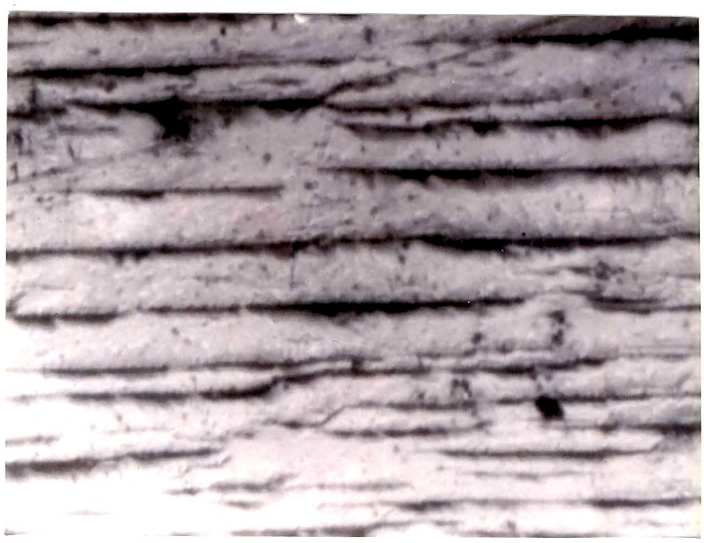


Fig. 8 **X 200**

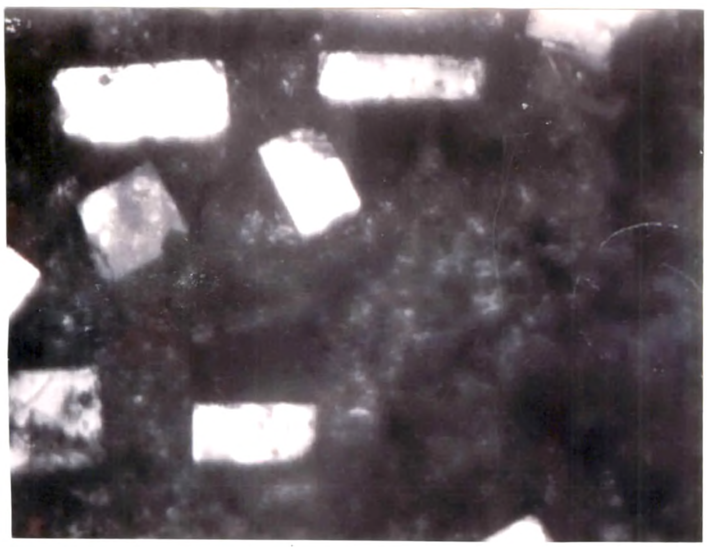


Fig. 9 X 250

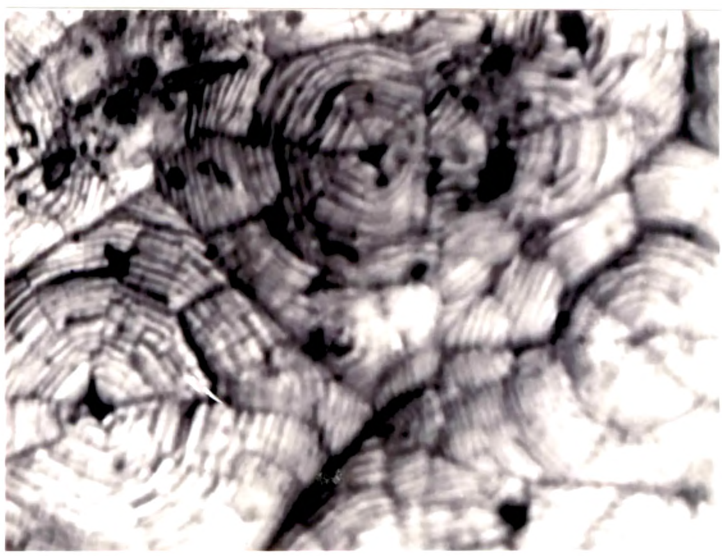


Fig. 10 X 400

nearly hexagonal shape nearest to the centers; while radiating out they assume approximately circular shapes. These may be interpreted to be a result of thermal instabilities associated with Se as an impurity responsible to nucleate these structures.

Interestingly when the same crystals are grown with large number of zone levelling passes the type of features described above are not at all obtained. On the other hand, striations perpendicular to the ingot axis are observed as in the case of $InBi_{1-x}Sb_x$ crystals. One example is shown in Figure-11. These facts support the improvement of homogeneity and crystal perfection due to large number of zone levelling passes as stated earlier.

CRYSTAL GROWTH BY SYRINGE PULLING METHOD :

Because of low melting point of the material the author has also tried the syringe pulling method to grow $InBi_{0.8}Sb_{0.2}$ single crystals as described below.

The ingot was prepared in the usual way and it was broken into small pieces and transferred to a porcelain crucible. Due to the low melting point, a gas burner flame can easily melt the material and hence the crucible was kept over a burner flame for melting the material. A corning glass syringe of 5ml capacity was kept vertically on a stand beside the burner as shown Figure-12. When the melt temperature

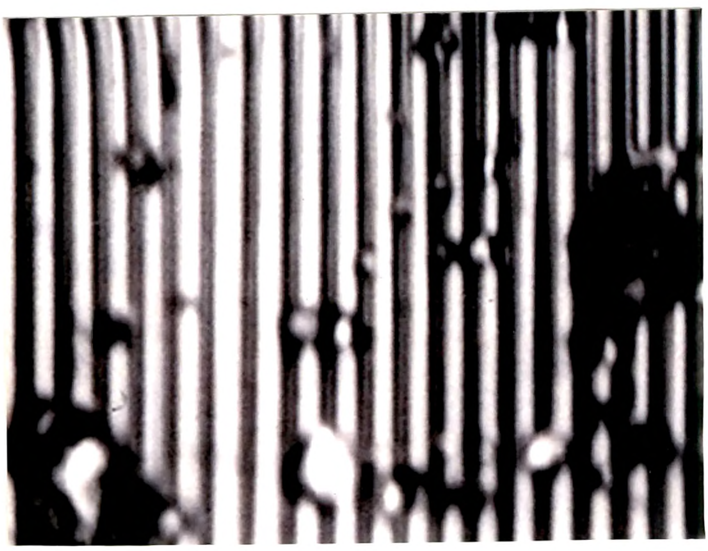


Fig. 11 **X 200**

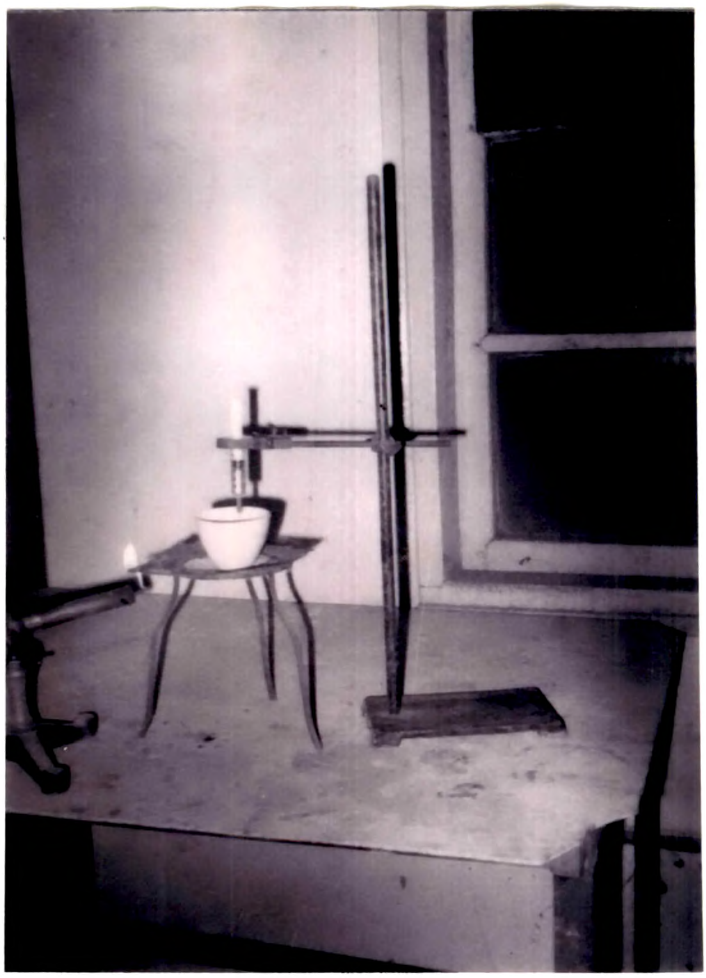


Fig. 12

reached around 150 ^{0}C, the oxide layer formed on the surface of the melt was scraped out and immediately the syringe mouth was dipped into the melt. The melt was sucked in manually within 30 seconds followed by a quick attachment of the stainless steel needle. Then the melt was allowed to cool freely to room temperature, which took about 10 minutes. Finally, the syringe was broken carefully and the grown crystal was taken out. It was observed that, the cylindrical surface of the crystal so obtained had bright shining. The crystal was then cleaved at ice temperature. The cleavage surface was found lustrous, smooth and mirror like and the cleavage plane (001) was found to be parallel to the vertical syringe axis. The crystal could be cleaved with single gentle tap of the blade right across the whole length. Obviously, in this method, the stainless steel needle serves as the heat sink and site of nucleation. The rest of the syringe system being non-conducting effectively provides unidirectional solidification. Almost all the crystals grown by this method were found to have the same preferred orientation. Fig.13 shows a typical as grown crystal which was obtained by this method. The counter parts of oppositely matched cleavage faces are shown in Fig.14.

As shown in Fig.14, the features on oppositely matched cleavage surfaces are in an exact one to one correspondence. The cleavage plane is shiny, perfectly plane containing very few cleavage lines and reflects good quality of the crystal. Although these crystals were not used for any

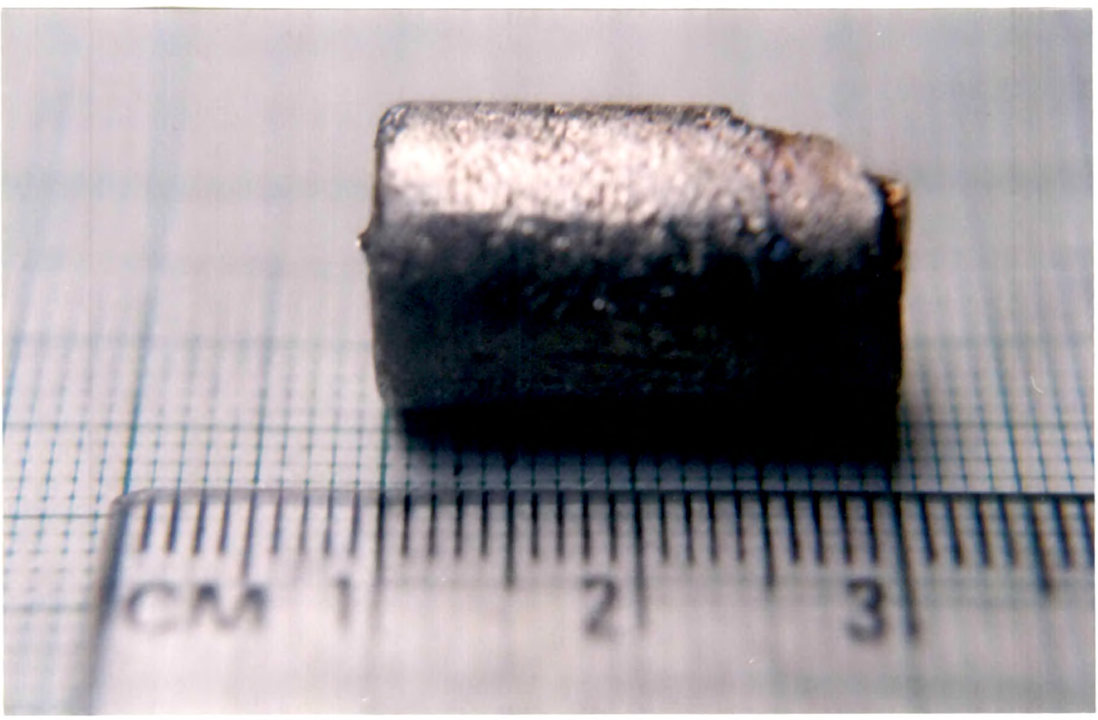
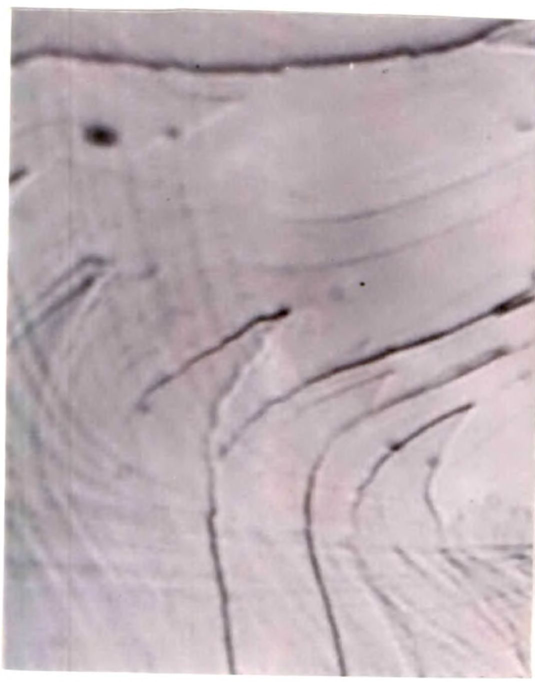


Fig. 13



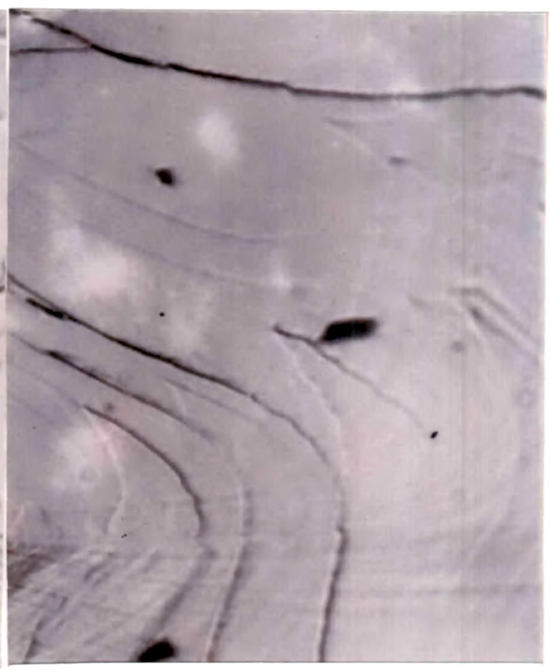


Fig. 14(a) X 100 Fig. 14(b) X 100

other investigations (due to oxide content), their dislocation densities were measured and found to be of the same order as in the case of crystals grown by zone – melting.

CONCLUSIONS :

(1) The $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ single crystals can be successfully grown by the zone – melting method. ($x = 0.2, 0.3, 0.4$).

(2) With increasing Sb/Se concentration the dislocation density of the crystal increases. However the over all perfection of Sb containing crystals is better.

(3) On increasing zone levelling passes the perfection of crystal increases.

(4) Using syringe pulling technique crystals of preferred orientation and of good quality can be obtained.

(5) The well-known growth striation characteristic of alloy crystals is obtained on crystals grown with large number of zone levelling passes. These together with the triangular features observed on the as grown free surface indicate layer mechanism of growth probably involving (111) plane.

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