CHAPTER- 6

CRYSTAL GROWTH OF $Bi_{1-x}Sb_x$ SINGLE CRYSTALS

Single crystals of Bi-Sb containing Antimony concentration varying from at 5% to at 30 % were grown by zone melting method. The perfection of the crystals was judged using dislocation etching. Several Research groups have investigated the use of Antimony as a surfactant during the growth of III-V compound semiconductors [1,2].

In the present work, Bi-Sb alloy crystals containing 5% at. to 30 at.% of sb were grown from melt by zone-melting method[3] described in chapter-5. Many factors are involved in the technique for successful results. The most important controlling factors are purity of the constituent metals, the effect of premixing the constituent metals, the number of passes in zone-leveling procedure, temperature gradient in the specimen and in the furnace and the speed of growth of single crystals[4,5,6].

The low melting temperature makes it difficult to achieve a large thermal gradient at the crystal growing interface, except by forced cooling. Forced cooling may result in excessive cracking, because the crystals are elastically anisotropic. The sell liquid diffusion coefficient has been estimated to be between 2 X 10^{-5} cm^2/sec and 3 X 10^{-5} cm^2/sec at 300°c. In order to grow homogeneous alloy single crystal, it is necessary to start with a relatively homogeneous solid charge. The mixing of component metals presented a good deal of difficulties because, it was found that there was a distinct tendency for an antimony rich layer to form at the surface of the crystal, due to the significantly lower density of antimony as compared to that of bismuth.

Bismuth and Antimony each of 99.999 % purity (5 N purity) were purchased from Nuclear Fuel Complex, Hyderabad, India. The stoichiometric amounts of 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 630 ^{0}C for thorough mixing. 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 $Bi_{1-x}Sb_x$(X=0.05,0.1,.0.15,0.20,0.25,0.30) alloys 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 figure 1. First the ingot was zone levelled. The temperature gradient across the two solid – liquid interfaces was obtained to be about 65 ^{0}C / cm by controlling the furnace temperature within $\pm$ 1 ^{0}C, giving a zone length of about 1-2cm.

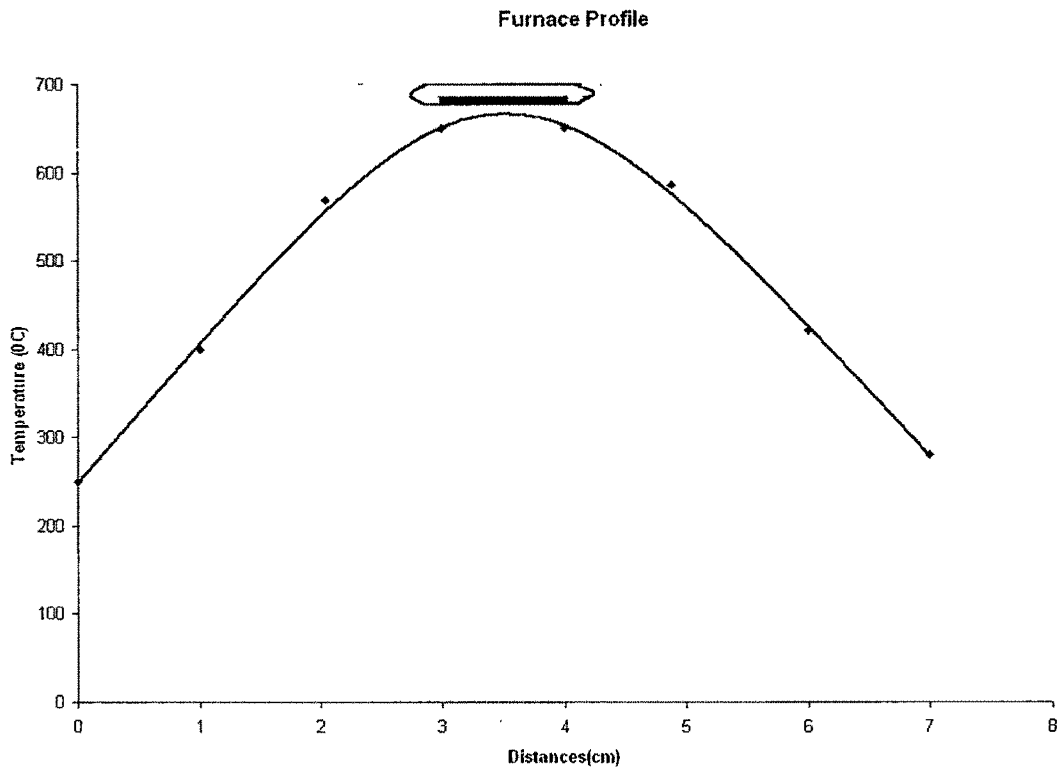

Figure- 1 Profile of furnace (Temperature gradient 65 ^{0}C/ cm)

To level off impurities, 10 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 0.3 were grown at the same growth velocity and temperature gradient. The quality of the crystals obtained was judged by examining the cleavage surfaces and obtaining dislocation density. ?

EFFECT OF IMPURITY CONCENTRATION AND GROWTH VELOCITY ON CRYSTAL PERFECTION:

A number of crystals of $Bi_{1-x}Sb_x$(X=0.05,0.10 ,0.15,0.20,0.25,0.30) were grown under this gradient at different growth velocities and the average dislocation density in each case was as shown in Table- 1. The dislocation echant consisting of 4 part nitric acid (A.R. Quality, 70%) + 7 part tartaric acid (saturated solution) + 1 part water was applied for about 10 sec. The cleaning and rinsing of etched specimens was done using methanol. The etchpit count was carried out under optical microscope. It can be seen from the table that the crystals obtained at different growth velocities are of good general perfection with dislocation density of the order 10^4 cm^{-2}. The dislocation density does show a systematic dependence on growth velocity. Further, it is observed that the perfection of the crystals increases as number of zone passes increases as shown in Table -2.

Table-1

Name of the material	Growth velocity cm/hr	No. of crystals grown	Cleavage Angle w.r.to growth axis	Dislocation density cm^{-2}
$Bi_{0.95}$ $Sb_{0.05}$	0.5	4	5	$2.7x10^4$
	0.9	3	11	$4.1x10^4$
	1.5	3	24	$6.3x10^4$
$Bi_{0.90}Sb_{0.10}$	0.5	3	7	$3.3x10^4$
	0.9	3	15	$5.0x10^4$
	1.5	2	37	$7.4x10^4$
$Bi_{0.85}Sb_{0.15}$	0.5	2	10	$3.8x10^4$
	0.9	2	21	$5.8x10^4$
	1.5	2	40	$8.0x10^4$
$Bi_{0.80}Sb_{0.20}$	0.5	3	13	$4.1x10^4$
	0.9	2	26	$6.0x10^4$
	1.5	3	45	$8.3x10^4$
$Bi_{0.75}Sb_{0.25}$	0.5	2	17	$4.3x10^4$
	0.9	3	30	$6.2x10^4$
	1.5	3	51	$8.6x10^4$
$Bi_{0.70}Sb_{0.30}$	0.5	3	22	$4.4x10^4$
	0.9	2	38	$6.3x10^4$
	1.5	2	60	$8.8x10^4$

Table-2

Material	Number of passes	Dislocation Density (cm^{-2})
$Bi_{0.95}Sb_{0.05}$	10	$4.0x10^4$
	25	$2.7x10^4$
$Bi_{0.90}Sb_{0.10}$	10	$5.2x10^4$
	25	$3.3x10^4$
$Bi_{0.85}Sb_{0.15}$	10	$5.9x10^4$
	25	$3.7x10^4$
$Bi_{0.80}Sb_{0.20}$	10	$6.4x10^4$
	25	$4.1x10^4$
$Bi_{0.75}Sb_{0.25}$	10	$6.9x10^4$
	25	$4.7x10^4$
$Bi_{0.70}Sb_{0.30}$	10	$7.3x10^4$
	25	$4.9x10^4$

It was found that at high growth velocity the (namely,1.5 cm/hr) solid-liquid interface bears irregularly shaped structures forming randomly oriented , pattern observed in Figure 2. In such cases, randomly oriented triangular facets of unequal size were observed on the top and cylindrical surfaces of the crystal as shown in Figure 3. For the same growth velocity, dendritic features were also observed on top free surface of the crystals, These are shown in figures 4,5,6.

When growth velocity is small, 0.5 cm/hr, we observed regular cell structures on solid-liquid phase (figure 7,8). Frequently, triangular facets on top free surface were observed as shown in figure 9. A few samples exhibited striations on top free surface, shown in figure 10. These are supposed to be associated with small transient thermal fluctuations which cannot be usually avoided.[5,6]

Figure 11 shows an optical micrograph of a cleaved surface. The triangular layer features indicate the surface orientation as to be consistent with symmetry. After deep polishing using dislocation etchant, same features are observed in figure 12, 13(a), 13(b). These observations indicate that crystals grow by layer mechanism.

Figures 14 and 15 shows an optical micrograph of oppositely matched cleavage plans of an ice cleaved crystal which was obtained at 0.5 cm/hr growth velocity. The matching of cleavage lines in near one to one correspondence indicates the single crystalline character. Figures 16 and 17 show faceted structures observed on top free surface of crystals. These are reported on

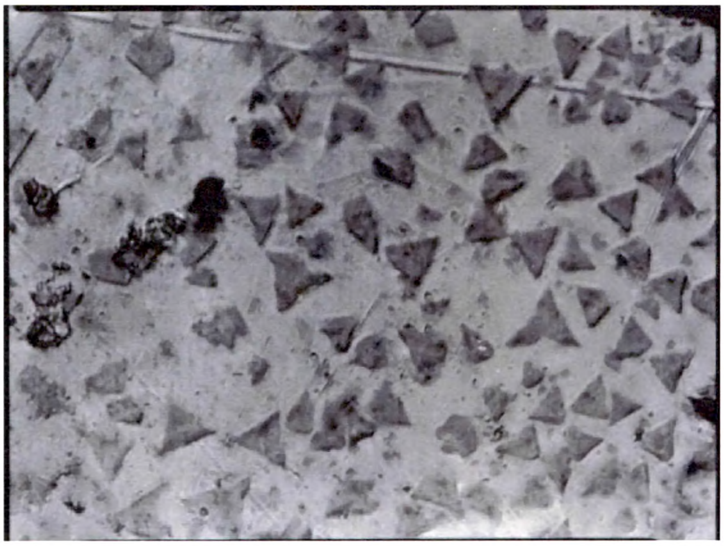

Figure-3 [X= 800]

Figure-4 [X= 300]

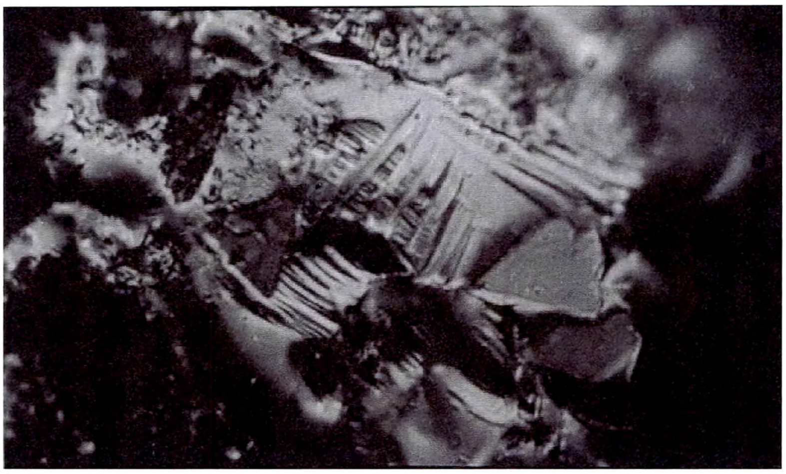

Figure-5 [X= 300]

Figure-6 [X= 500]

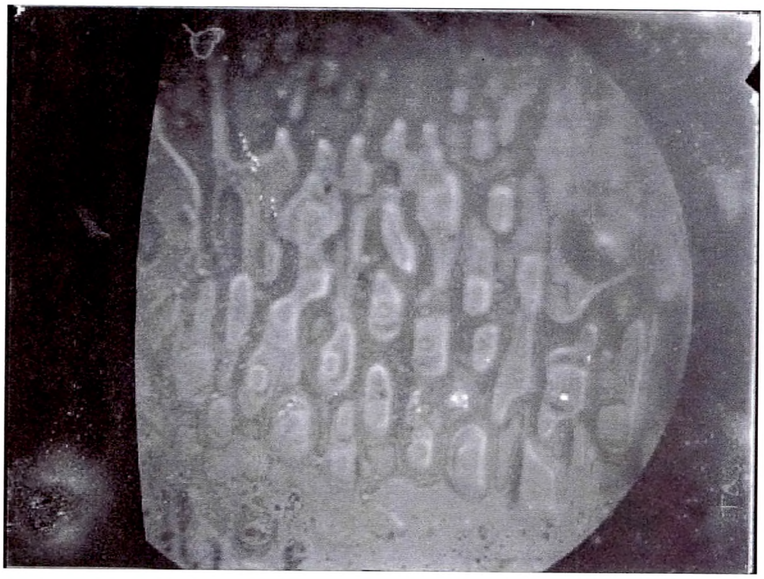

Figure-7 [X= 300]

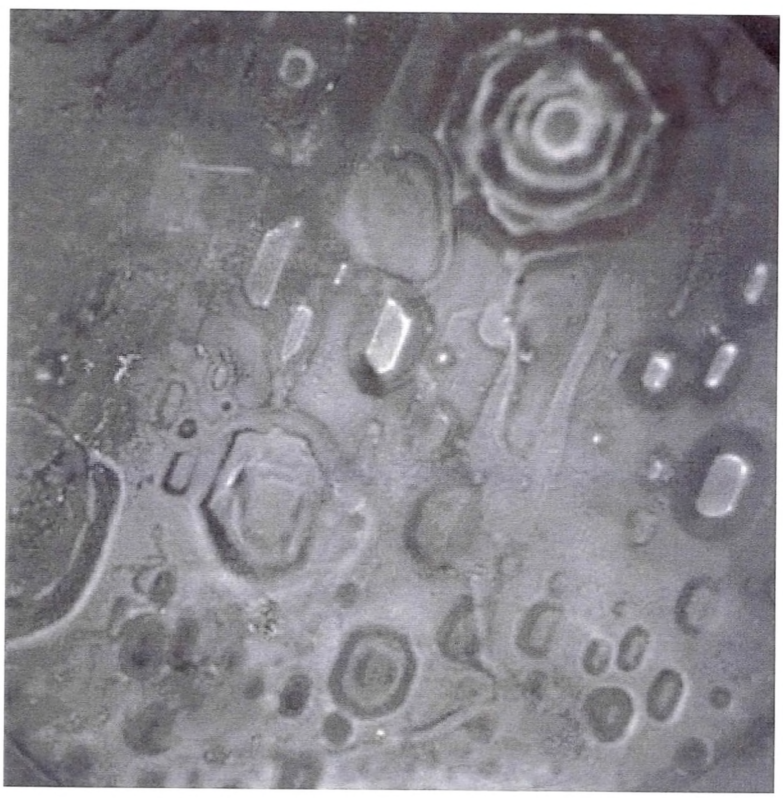

Figure-8 [X= 500]

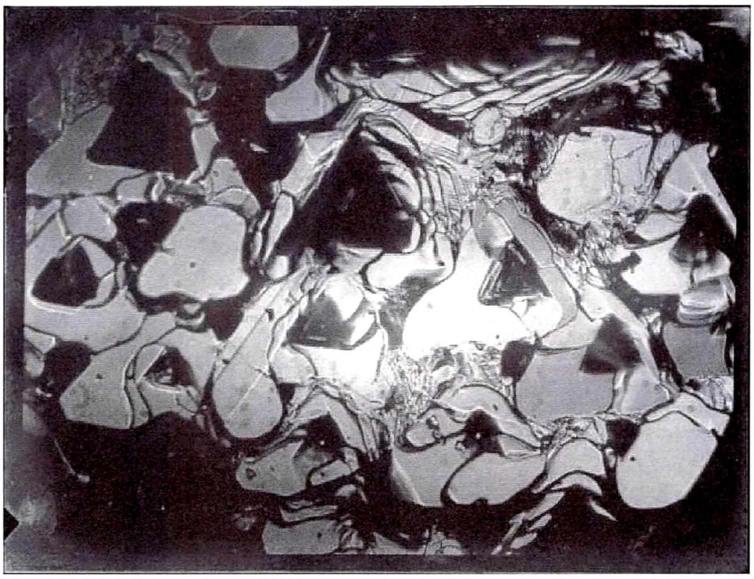

Figure-9 [X= 300]

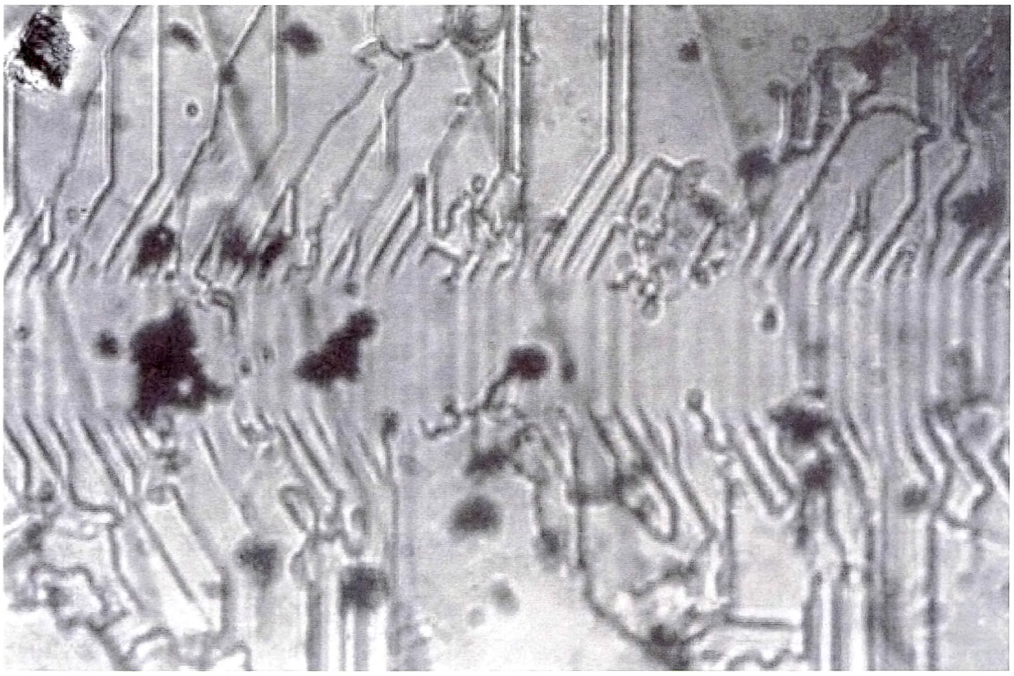

Figure-10 [X= 200]

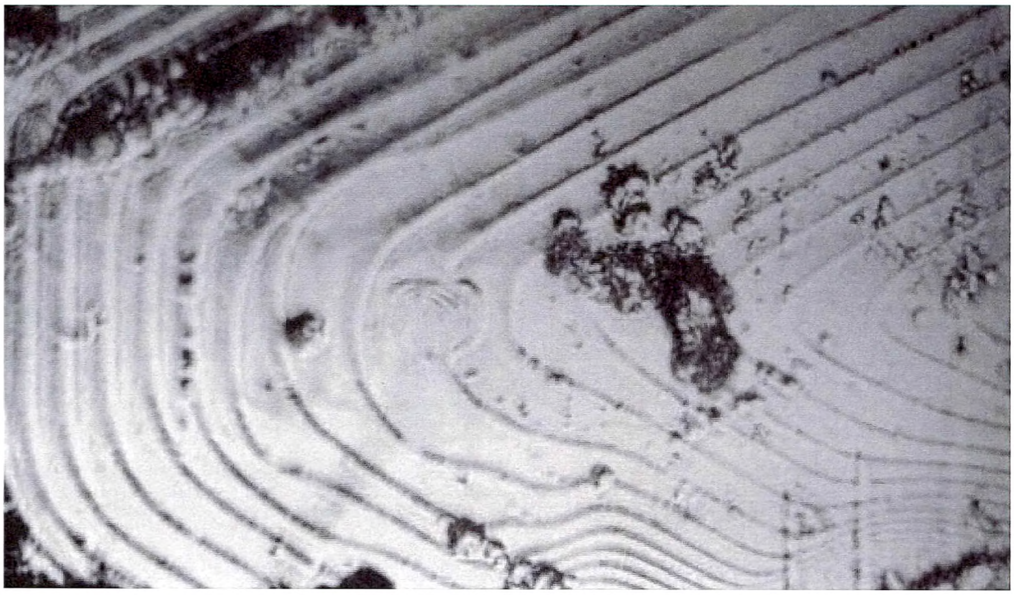

Figure-11 [X= 500]

Figure-12 [X= 500]

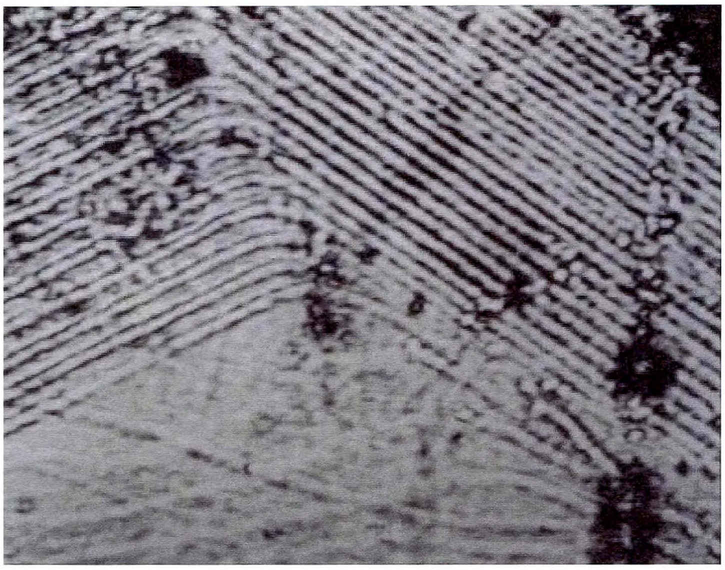

Figure-13(a) [X= 500]

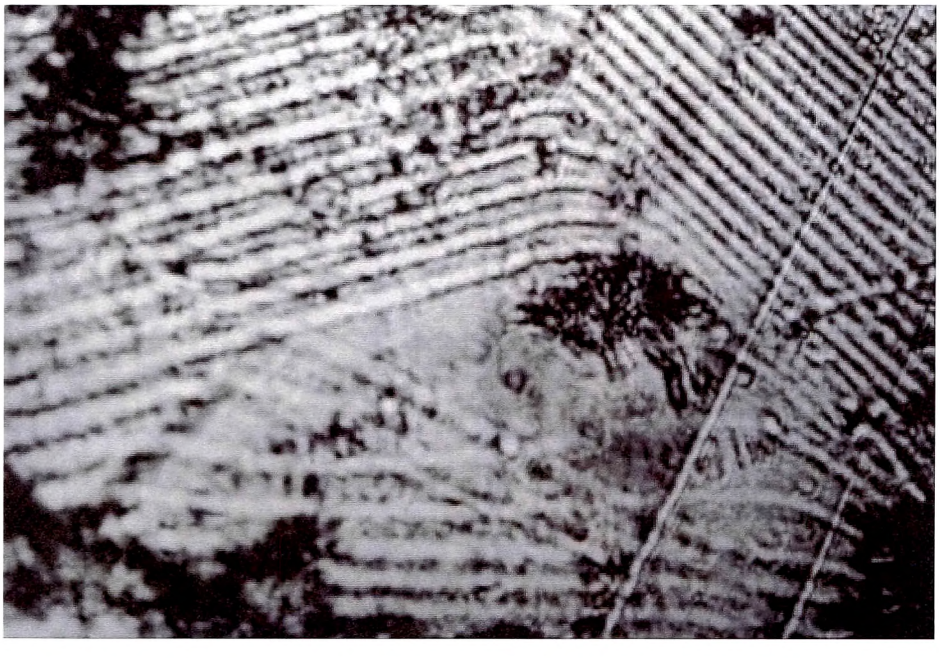

Figure-13(b) [X= 500]

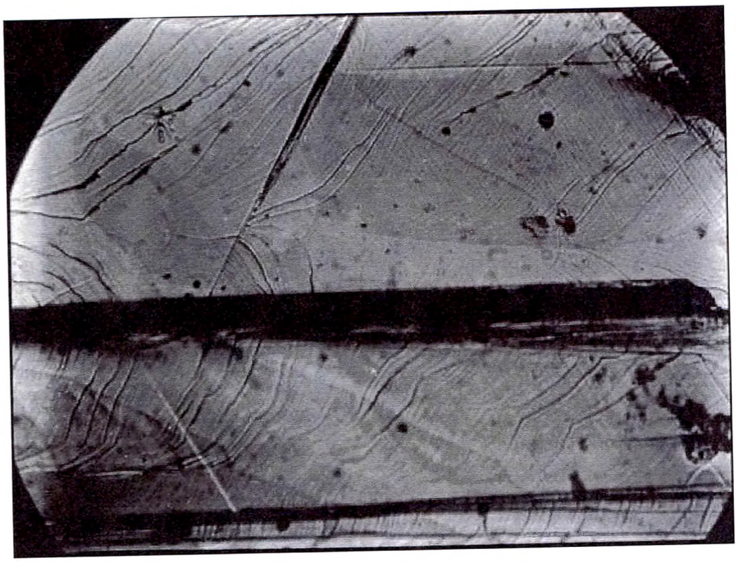

Figure-14 [X= 200]

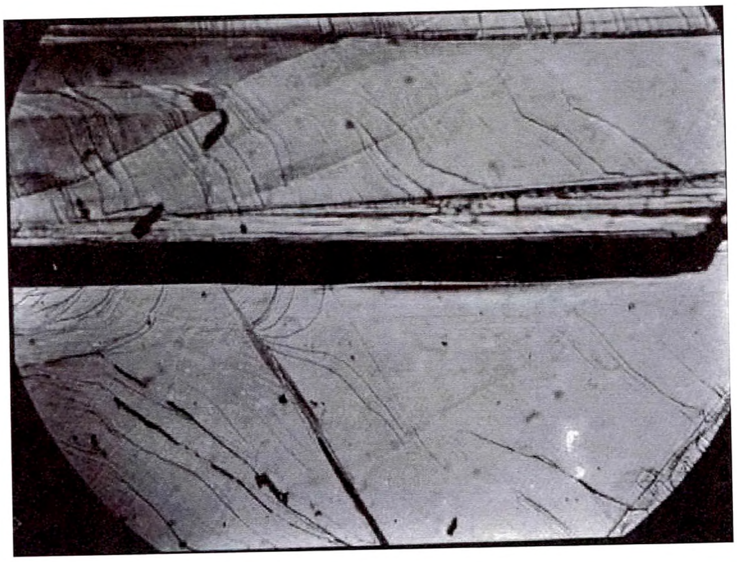

Figure-15 [X= 200]

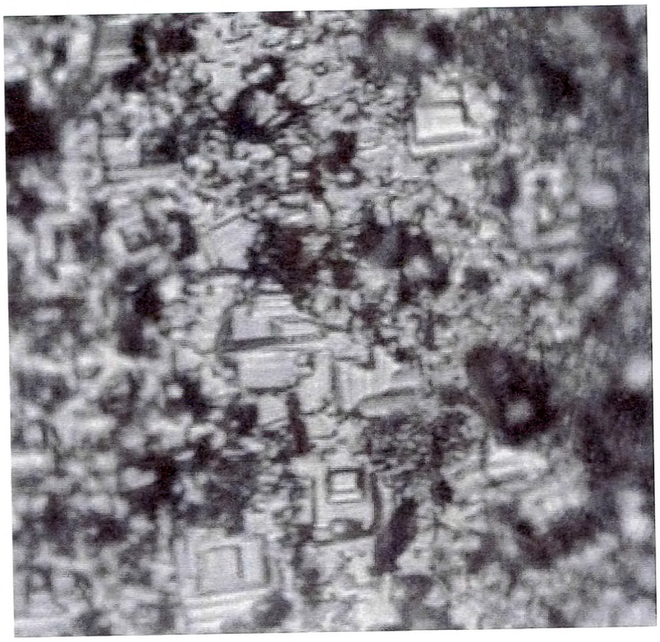

Figure-16 [X= 500]

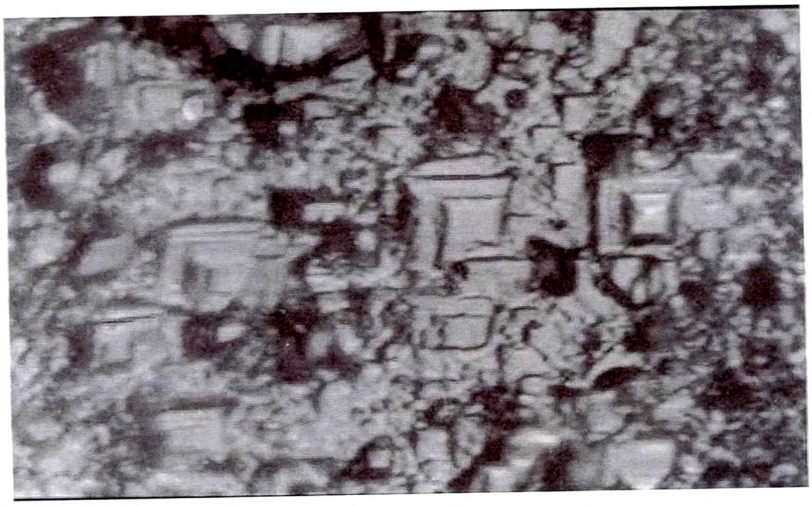

Figure-17 [X= 300]

Conclusions:

1. Good quality crystals of $Bi_{1-x}Sb_x$ can be obtained by the Zone melting technique at zone travel rate 0.5 cm/hr and temperature gradient 65°C/cm.

2. The crystal perfection of $Bi_{1-x}Sb_x$ (x= 0.05,0.10, 0.15,0.20,0.25,0.30) decreases as the growth velocity increases. The dislocation densities are found to be in the range 10^4 cm^{-2} in the crystals grown under the above stated conditions.

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