PART - B

CHAPTER – 6

CRYSTAL GROWTH AND DISLOCATION ETCHING

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CRYSTAL GROWTH AND DISLOCATION ETCHING

Section - I

Crystal Growth of $In_x Bi_{2-x} Te_3$ Crystals

The most widely used method for growing bulk crystals of V – VI and IV – VI compounds is the Bridgman-Stockbarger technique [1,2]. In the vertical Bridgman-technique, the compound is melted in a vacuum sealed ampoule placed inside a vartical furnace. The furnace consists of two halves. These two halves are separated by a baffle. The upper part of the furnace is kept at a temperature more than melting point of the material. In the growth process, the melt in the lower tip of the ampoule is frozen first by lowering it slowly through the temperature gradient[3] defining the effective change from the liquid to solid phase and it is here that single nucleation event is required to grow subsequently as a single crystal through the rest of the material as it solidifies. The tapered nerrow end of the ampoule or crucible favours single nucleation or one of the nuclei to survive and grow further with lowering of the ampoule and gradual solidification of the melt proceeds.

The formation of $Bi_{2-x}In_xTe_3$ mixed crystals was reported for the first time by Rosenberg and Strauss in 1961 [4]. The growth was achieved in a vacuum

sealed quartz ampoule containing the charge and placed in a vertical furnace which had a temperature gradient of about 15°C/cm. Jansa et al [5] have successfully grown $Bi_{2-x}In_xTe_3$ crystals (x = 0.1) by Bridgman method. Lostak et al have grown $Bi_{2-x}In_xTe_3$ (x = 0 to 0.66) single crystals using a modified Bridgman method at a rate of 1.3 mm/hr. [6]. They have also studied crystal homogeneity by determining the indium content and variation of Seeback coefficient in the directions perpendicular and parallel to the crystal axis.

Single crystals of InBi, Bi-Sb, SnS, SnSe, Bi-Te, $SnSe_2$ have been grown in this laboratory using different methods of crystal growth from melt such as Bridgman, Czochralski, Zone melting and Chalmers methods by various workers (Desai C.F., Shah R.C., Jani T. M., Vyas S. M., Gireesan K.)[7-11]. In the present work the crystals of $In_xBi_{2-x}Te_3$ were grown with an aim to study the effect of indium as an impurity on crystal growth with regard to crystal orientation and perfection and other properties, especially, hardness, etching and optical properties.

Crystal Growth by Zone Melting Method :

Indium, bismuth and tellurium of 5N purity supplied by Nuclear fuel complex, Hyderabad, were weighed to stoichiometric proportions, up to 10 microgram accuracy using a semimicrobalance and sealed under a vacuum of

10^{-5}Pa in a quartz ampoule. The ampoule was kept in a horizontal furnace at 700°C and rocked for 48 hours and cooled slowly to room temperature. This process usually produces a fairly homogeneous ingot. The temperature was measured and controlled with a proportional temperature controller within ±5°C using Chromel-Alumel thermocouple. The $Bi_{2-x}In_xTe_3$ compound prepared as above was used for growing single crystals by zone melting method. The starting ingot was about 6 cm in length and 0.8 cm in diameter. First the ingot was zone levelled. The temperature gradient across the two solid-liquid interfaces was about 70°C/cm giving a zone length of about 8mm to 10mm with a maximum temp. 650°C. 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 ranged from 0.4 cm/hr to 2.0 cm/hr.

The crystals were characterised using x-ray diffraction analysis. The powder diffraction patterns of three compounds are shown in Fig.1,2,3. The pattern consists of well-defined sharp diffraction lines. The identification of the peaks in diffraction intensity was made using a JCPDS data card [12]. The peaks not accompanied by name are all of Bi_2Te_3. The index assignments are indicated

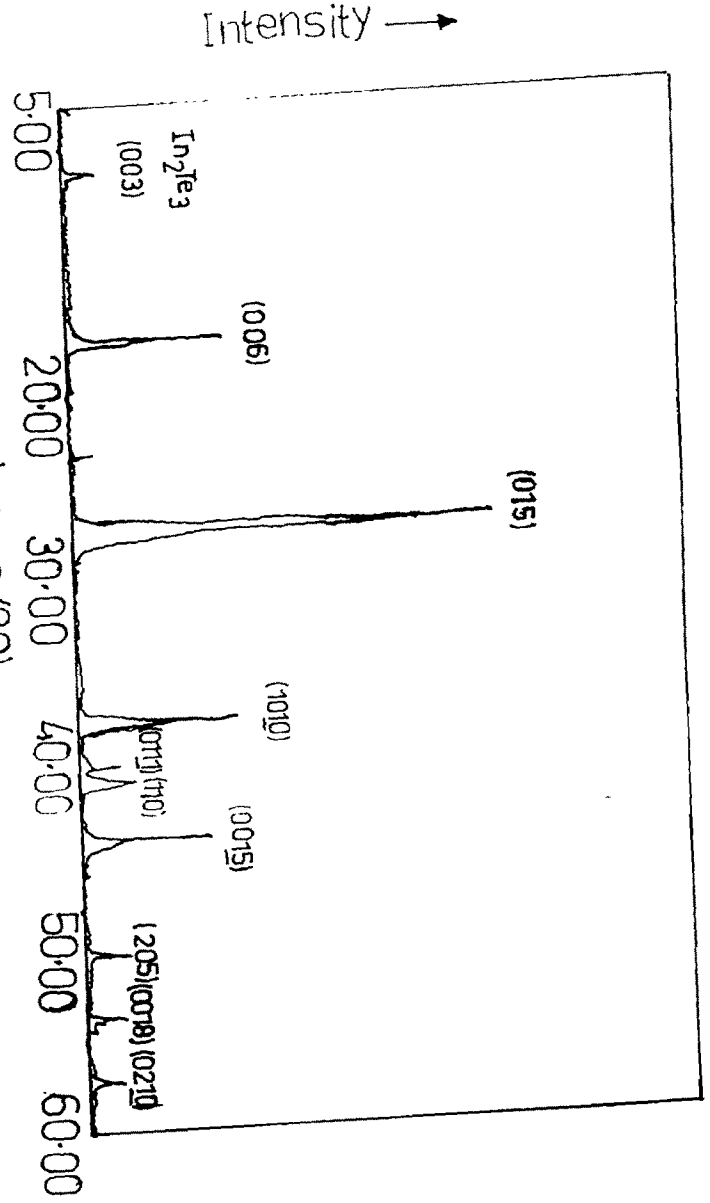

Fig.1. XRD for $In_{0.1}Bi_{1.9}Te_3$ crystal.

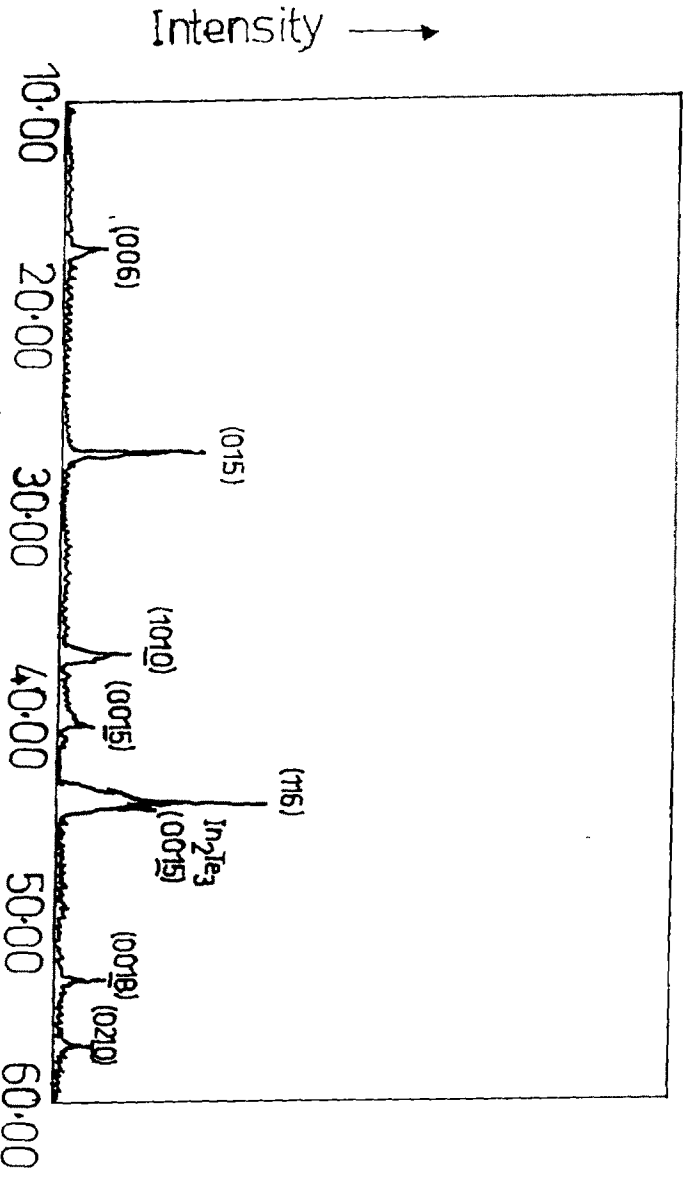

Fig.2. XRD for $In_{0.2}Bi_{1.8}Te_3$ crystal.

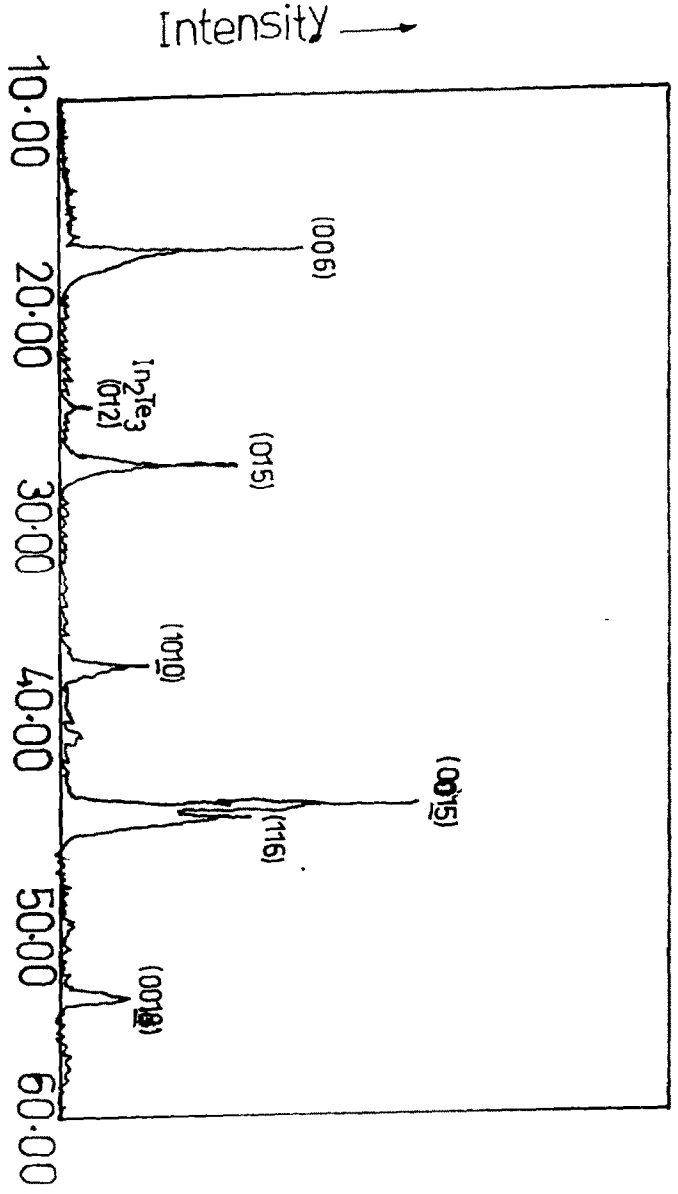

Fig.3. XRD for $In_{0.5}Bi_{1.5}Te_3$ crystal.

on the major peaks in the respective plots. The observed and the JCPDS file values are found to be in good agreement Bi_2Te_3 has a rhombohedral structure and its hexagonal unit cell is often used in crystal structure studies. Y. Feutelaic et al[13] have reported the values of lattice parameters of the hexagonal cell, as a = 4.395 Å and c = 30.44 Å, in good agreement with our calculated parameters : a = 4.392Å and c =30.54Å, a= 4.364 Å and c =30.126Å and a =4.354Å and c =30.24 Å respectively, for $In_{0.1}Bi_{1.9}Te_3$ and $In_{0\,5}\ Bi_{1\,5}\ Te_3$, $In_{0\,2}Bi_{1\,8}Te_3$ and $In_{0\,5}Bi_{1\,5}Te_3$ single crystals.

Crystal Orientation :

The indium concentration in the ingot was varied from x = 0.1 to 0.5 and the crystals were grown at various growth velocities ranging from 0.4 cm/hr to 2.0 cm/hr. for each concentration. Crystals obtained after ten zone levelling passes and the final growth pass, were cleaved on ice to minimize deformation due to the cleavage process. Since the crystals were in rod shapes, the orientation of the crystal was measured as the angle made by the cleavage plane (0001) with the ingot axis.

For each growth velocity and concentration, minimum three crystals were grown. The results obtained were averaged. Table-1 lists the data of the single crystals obtained in each case and the observed orientations.

The phenomenon of preferred orientation can be observed in the Table-1. The orientation significantly depends on the growth velocity and for each concentration; as the growth velocity increases, the cleavage plane tends to orient parallel to the ingot axis.

A careful observation of the table indicates that the orientation remains more or less the same at a given growth velocity, irrespective of indium concentration. For each growth velocity and composition the average dislocation density was measured. For this, the etchpit count method was applied, using dislocation etchant to be described in Sec.II of the present chapter. From Table–2 it can been seen that the crystal perfection decreases with increase in growth velocity and increase in concentration. The perfection in general is fairly good up to a growth velocity 1cm/hr. However for the higher In concentration, perfection, even at low growth velocity is not satisfactory. This can be improved by increasing number of zone passes, as discussed below.

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 levelling is very effective in uniform distribution of impurity. As a result of the uniform impurity distribution, the zone levelling also improves the crystal perfection. This is because the differences in impurity

TABLE – 1

Name of Crystal	Growth Velocity cm/hr.	Angle made by the specimen axis with cleavage plane ($\pm 3^{o}$)
$In_{0.1}Bi_{1.9}Te_3$	0.4	18
	0.7	16
	1.0	13
	1.35	11
	2.0	5
$In_{0.2}Bi_{1.8}Te_3$	0.4	23
	0.7	19
	1.0	15
	1.35	11
	2.0	7
$In_{0.5}Bi_{1.5}Te_3$	0.4	20
	0.7	18
	1.0	14
	1.35	10
	2.0	6

Table – 2

Name of Crystal	Growth Velocity cm/hr.	Number of passes given	Average Dislocation Density cm^{-2}
$In_{0.1}Bi_{1.9}Te_3$	0.4	10	1×10^4
	0.7	10	1.3×10^4
	1.0	10	1.9×10^4
	1.35	10	2.2×10^4
	2.0	10	3.6×10^4
$In_{0.2}Bi_{1.8}Te_3$	0.4	10	1.35×10^4
	0.7	10	1.7×10^4
	1.0	10	1.9×10^4
	1.35	10	2.3×10^4
	2.0	10	4.7×10^4
$In_{0.5}Bi_{1.5}Te_3$	0.4	10	2.0×10^4
	0.7	10	2.7×10^4
	2.0	10	7.8×10^4

concentration along the crystal can produce fairly larger 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[14]. Thus since number of zone passes affects homogeneity and hence perfection of crystals, at least three crystals were grown with large number of alternate zone levelling passes, viz 20 and 30. For these growths, the growth velocity and indium concentration were kept constant at 1.35 cm/hr and x = 0.2 respectively. Table-3 gives the measured average dislocation density of the crystals. It was observed that as the number of zone passes increases the dislocation density decreases.

Typically the best crystals were obtained after 30 passes, having dislocation density 1.7×10^4 cm^{-2}. Fig.4(a), 4(b) show the cleavage counter parts in oppositely matched orientation, observed in the case of a crystal grown with 30 zone passes. The striking planarity of the surface with few observable cleavage lines indicate good perfection of the crystals. The top free surfaces of the as-grown crystals were observed under optical microscope. Some interesting features were observed. Fig.5 shows frequently observed typical feature consisting of concentric layers. Such layers indicate that the crystal probably grows by layer mechanism [15,16].

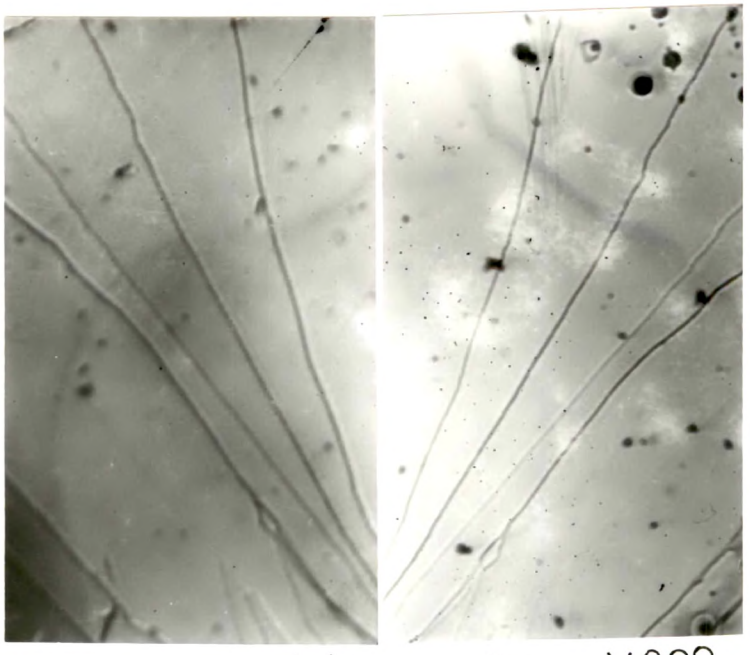

Fig.4 (a) (b) X200

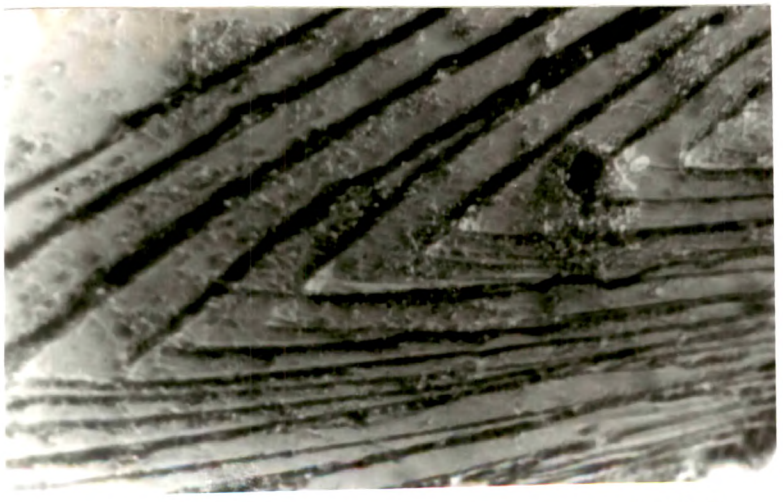

Fig.5 X400

Table – 3

Growth velocity cm/hr.	Number of zone Passes	Average dislocation density cm^{-2}
1.35	10	2.3×10^4
	20	2.0×10^4
	30	1.7×10^4

Fig.6 shows a photograph of features observed on crystals grown at 2 cm/hr. The features resemble dendrite features. Such dendrites are characteristics resulting from thermal instabilities [17] At higher growth velocities thermal instabilities are expected. This is also evidenced by poor quality of crystals indicated by higher dislocation density obtained at higher growth velocity

Crystal Growth by Bridgman Method :

$In_xBi_{2-x}Te_3$ ingots were prepared in the same way as for the zone melting growth. For the Bridgman growth, the vertical furnace described in ch.4 was employed to grow the crystals The temperature profile of the furnace is shown in Fig 7. The temperature gradient and ampoule lowering rate were 45°C/cm and 0.4 cm/hr., respectively. The ingot was kept in the nearly uniform temperature zone at about 650°C. It was retained at this position for 10 to 12 hours. Then the ampoule was lowered through the gradient to reach the bottom of the furnace. The top free surface was observed to exhibit the features shown in Fig.8. These are all triangular in shape and with the same orientation. In view of the rhombohedral structure of the crystal, these features can be said to be associated with the crystal symmetry. Hence the mere occurrence of these features is indicative of single crystalline character of the ingot. These features might have been caused by the phenomenon of thermal etching during the growth process

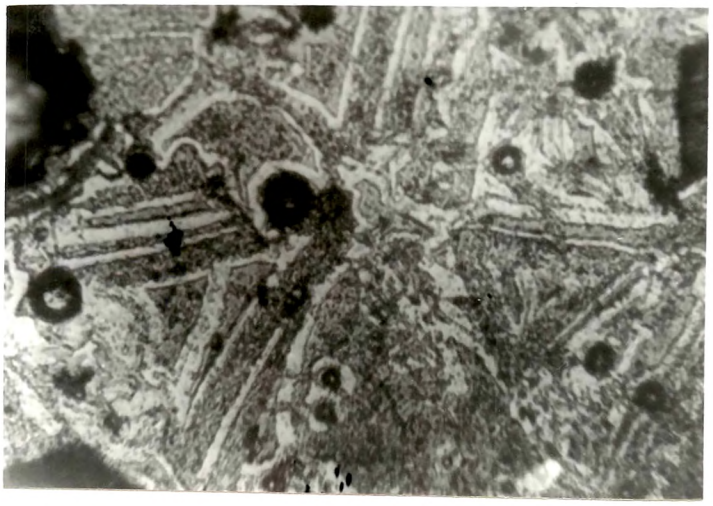

Fig.6 X 330

Fig.7. Temperature profile of Bridgman furnace.

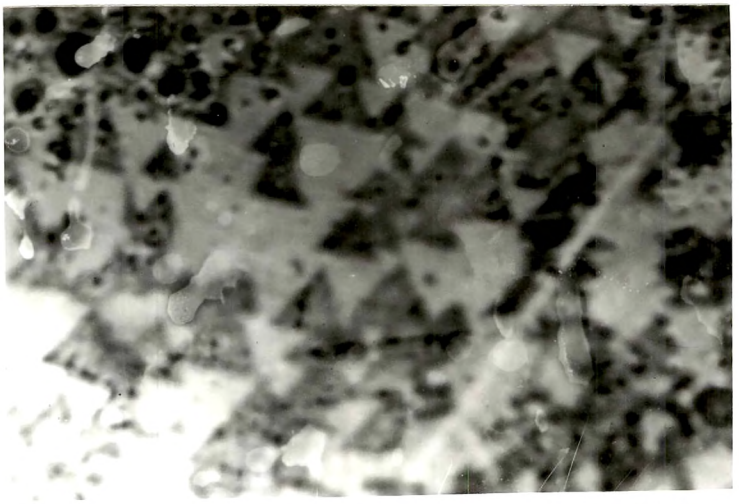

Fig.8 X280

Vapour over growth of $In_{0.2}Bi_{1.8}Te_3$ Crystals :

Some annealing experiments were carried out on the cleavage slices required for the hardness study (Ch.7). There were some interesting observations obtained on these samples also. These are described below.

The cleavage slices each of 2mm thickness, were vacuum sealed in a pyrex tube under a pressure of 10^{-3} Pa, and were placed in a furnace at the temperature of ~375°C for different periods of time. They were then slowly cooled to room temperature at a rate of ~20°C/hr The cleavage face of the sample was then observed under an optical microsope.

On the sample treated at 375°C for 12 hours, triangular features were observed and for the same temperature but anneal time of 24 hours, hexagonal features were observed. Typical examples are shown in figures 9 and 10. It is worthwhile to note that though the features in Fig.10 are hexogonal and have three fold symmetry consistent with the crystal structure. There features may be associated with recondensation of vapours produced by sublimation during annealing. It may be possible that the temperature of about 375°C may be favourable for the vapour growth of the crystals.

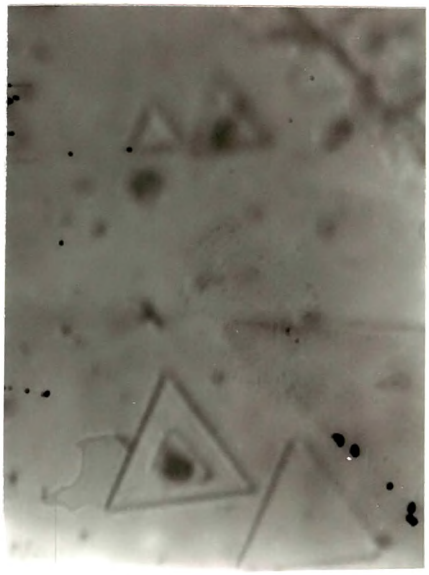

Fig.9 X430

Fig.10 X500

Section - II

Dislocation Etching of $In_x Bi_{2-x} Te_3$ Crystals

The work carried out and reported by the present author in this chapter, deal with the results from the chemical etching study of the $In_xB_{2-x}Te_3$ single crystals with x = 0.1, 0.2 and 0.5. No study on chemical etching of these single crystals has so far been reported [18-19].

Though many sophisticated analytical techniques for revealing dislocations are now available, the chemical etching technique is having special status among them because of its simplicity. Moreover, the method is quite rapid as compared to other methods. Chemical etching has a wide range of applications; it is used :

1) For revealing defects in the crystalline materials and to study the behaviour and mode of formation of dislocations.
2) For orientation determination in conjuction with optical goniometry.
3) For preparation of clean surface.
4) To obtain reproducible electrical properties of semiconductor.
5) To determine impurity distribution
6) For controlled removal of material.

The discussion which follows is confined to the use of chemical etching for studying dislocations.

For the formation of etch pits at dislocation sites, the etching rate along the dislocation line is very essential to be greater than that on the rest of the surface. It has been proposed that increase in the etching rate along a dislocation line is due to the strain field associated with the dislocation. Therefore, it is an accepted fact that chemical etching is a simple, rapid and valid method for revealing dislocations. This makes it a valuable tool for studying perfection and plasticity of crystalline materials.

Various methods have been employed to establish a relation between etch pits and dislocations.

1) Perfect matching of etch pits on matched cleaved surfaces.
2) Repetation of the pattern on successive etching which allows the tracing of dislocations to some depth within the crystal.
3) Introducing various types of plastic deformation and looking for corresponding increased etch pit density.

The inhomogeneities in the grown crystals are revaled by etching because reactions take place at inherently different rates at the inhomogeneity sites. The structural defects like point defects, line defects, inclusions, segregation etc. are selectively attacked by the etching reagent and as a consequence their precise locations are manifested finally by some visible etching characteristics, such as

cavities, striations, local decolouration etc. Before etching, many of the inhomogeneities and defects associated with the section of interest may be small in size and even entirely invisible. But during etching, the area occupied originally by certain of these inhomogeneities will increase in size beyond their original dimensions and eventually reach a size which will be visible and amenable to detailed study under a variety of techniques.

The successful application of etching depends upon several factors such as

1) The condition of the crystal surface that is to be etched.
2) Chemical composition of the etching reagent selected.
3) Temperature of the etching reagent.
4) The length of time for which the specimen is etched.

Etching reagent should possess the following characteristics.

1) The reagent should be such that it will give good all round results and reveal the greatest number and variety of structural characteristcs, defects and irregularities present. At the same time, it should be able to distinguish its effect from those produced by any of the etchants which can attack on only definite type of defects.
2) The composition of reagent should be simple and stable so that the concentration of reagent will not change appreciably upon standing or

during use at room temperature and also if possible, at moderately higher temperatures.

3) At a particular temperature, the regent should have constant characteristics, so that the etching condition can be easily reproduced. In the etching process the time of etching and the temperature are also important factors.

(a) Temperature of Etching :

The rate at which the etching regent attacks the specimen, depends on the temperature at which etching takes place The precise influence of temperature, however, varies according to the composition and previous history of the specimen. It is therefore desirable for obtaining reproducible results, to carry out etching experiments only at definite temperature.

(b) Time of Etching :

The etching time is perhaps one of the most important factors contributing to successful etching and attendant appearance of the structure enabling their detailed study possible with the help of optical techniques. For example, for short time of etching as compared to that appropriate for a particular material, the etched structure will not be completely developed nor will be sufficient

details revealed to permit accurate interpretation of the etched area. However, too long a time of etching is just as unsatisfactory as one too short, owing to details of the surface structure being thereby obscured to varying degrees and frequently some parts of the structure being completely obliterated. The time of etching depends on the conditions of the speciman and the temperature of the reagent.

4) The reagent, while acting on the specimen should not form products which would precipitate on the surface of the specimen considered, but must have such a composition that reaction products are immediately dissolved chemically or physically in the solution. They must possess closer affinity with the etchant than with the specimen.

5) The reagent should be non-injurious and non-toxic to the person conducting the work.

6) For orientation determination, the etchant should develop etch pits with plane faces accurately parallel to crystallographic planes of low indices. Looking to the above requirements of the etchant and the surface to receive it [i.e. in the present case, cleavage planes of $In_xBi_{2-x}Te_3$ for x = 0.1 to 0.5 single crystals] numerous trials were taken and it was found that the etchants developed by the present author possess most of the properties discussed above and were well suited for revealing dislocations

It is well known that, for metals, the necessary ingradients of an etchant are generally an oxidant and a complexant which may respectively, react with the specimen surface and dissolve the products formed. Mineral acids like HNO_3 and HCl and iodine and bromine are well known oxidants for etching of metals, alloys and intermetallics. In the present case, they were found to work well. It was also observed that the crystal surface in question has a high tendency to corrode and frequently to capture the reaction products, as also evident from the earlier reported results on etching. This fact poses a severe difficulty in developing a successful etchant. In the trials done by the author all the chemicals used were of AR grade and all the etching trials were carried out at room temperature on freshly cleaved surfaces.

Etchant for $In_{0.2}Bi_{1.8}Te_3$:

For the (0001) plane of $In_{0.2}Bi_{1.8}Te_3$ crystals, after numerous trails, an etchant was developed. This consists of saturated solution of I_2 in methanol, conc. HCl (70%) and HNO_3 (70%), which gives good results of dislocation etching. Some of the systematic stages of trials are presented in Table-4. Thus, the etchant consisting of 3 part of conc. solution of I_2 in methanol, 0.2 part of HCl and 0.2 part of HNO_3 is capable of producing well defined etch pits.

Table-4

Composition of Etchant	Etching Time	Remark
1) HCl (70%) 1part + H_2O 1part	30 Sec.	No etch pits observed
2) 1part HCl + 1part HNO_3 + 1part H_2O	30 Sec.	No etch pits observed
3) 1part HCl + 1part H_2So_4 + 1part H_2O	10 Sec.	No etch pits observed
4) $K_2Cr_2O_7$ in water	10 Sec.	No etch pits
5) 3part $K_2Cr_2O_7$ in water + HCl 1part	20 Sec.	No etch pits
6) 3part $K_2Cr_2O_7$ in water + HNO_3 1part	20 Sec.	No etch pits
7) 3part $K_2Cr_2O_7$ in water + H_2So_4 1part	10 Sec.	Corrosion of Surface
8) 3part $K_2Cr_2O_7$ in water + 1part HCl + 1part HNO_3(70%)	20 Sec.	No etch pits
9) Saturated Solution of I_2 in methanol	30 Sec.	No etch pits
10) 10part Saturated Solution of I_2 in methanol	30 Sec.	Spoils surface
11) 10part Saturated Solution of I_2 in methanol + 2part HNO_3(70%)	10 Sec.	Circular Pits were observe
12) 10 part saturated Solution of I_2 in methanol + 2part HNO_3 + 2part HCl (70%)	20 Sec.	ill shaped pits observed (Fig.11)
13) 5part saturated Solution of I_2 in + methanol 1part HNO_3+1part HCl(70%)	20 Sec.	irregular pits of unequal site.
14) 5part saturated Sol^n of I_2 in methanol + 0.5part HNO_3 + 0.3 part HCl (70%)	20 Sec.	Triangular pits of unequal size
15) 3part saturated Sol^n of I_2 in methnol + 0.3part HNO_3 + 0.3part HCL (70%)	30 Sec.	Triangular point bottomed pits (Fig.12)

Fig.11shows the etch pattern obtained with comp. (No.12) producing ill-defined etch pits. Decreasing HNO_3 to 0.3 parts and HCl to .3 parts gives point bottomed etch pits which are shown in Figure.12. The shape of the etch pits is also regular and nearly well defined triangular. Further, they have same orientation. In a region of crystal where there is high dislocation density, the etchant would give a close cluster of pits. A typical case is shown in Fig.13. As can be seen, at high magnification the individual dislocations in the cluster are distinctly revealed by the well defined etch pits.

It is essential to establish the reliability of a dislocation etchant. Therefore a few standard tests were carried out. One of the most important tests applicable for the cleavage surface is to establish one to one correspondence between the etch pits produced on the cleavage counter parts. Also this test itself is generally considered a quite adequate proof that the etch pits mark the sites where the dislocations intersect the surface.

Figure. 14(a), (b) show the etch patterns on the oppositely matched cleavage[16,21-22]. As can be seen there is one to one correspondence of etch pits on the counter parts.

The test of successive etching is based on the fact that a dislocation line cannot terminate within the crystal. Fig.15(a) and (b) show the etch pit pattern

Fig.11 X180

Fig.12 X250

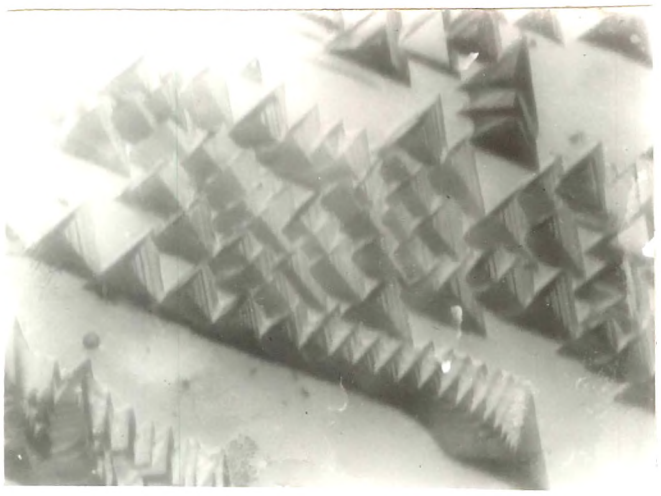

Fig.13 X400

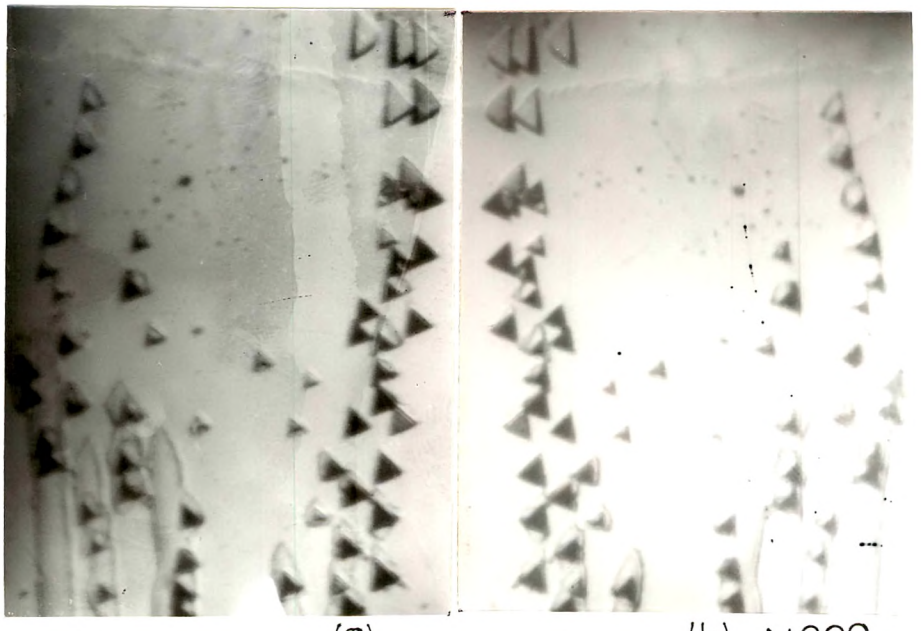

Fig.14 (a) (b) X200

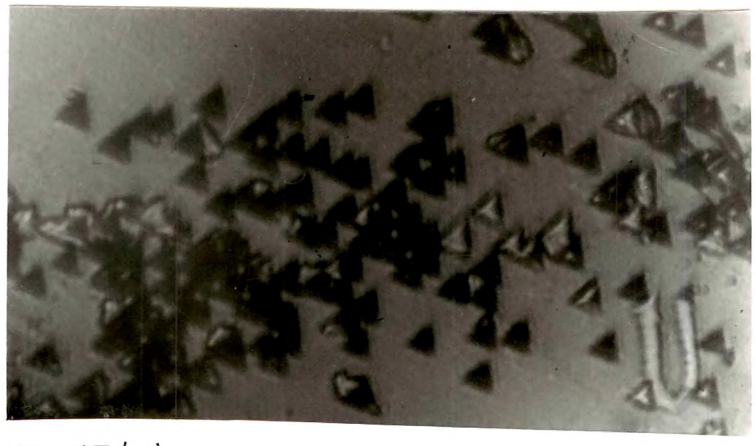

Fig.15 (a) X 250

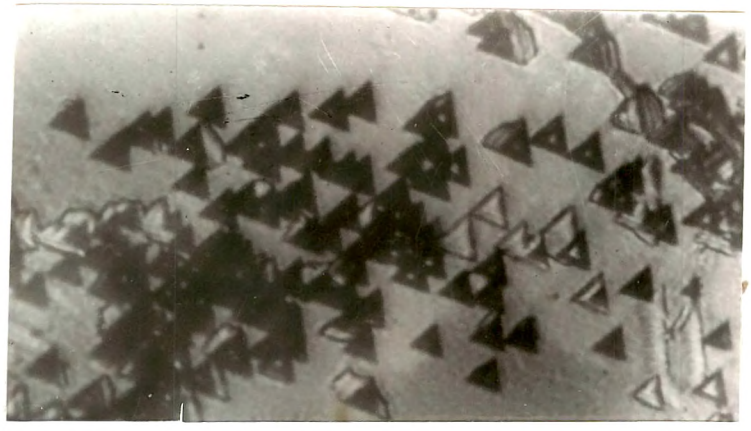

Fig.15(b) X 250

obtained on the same region on the same cleavage surface etched for 30s and additional 10 seconds, respectively, using this etchant. It can be seen that the pits have to some extent increased in size with the etching time, whereas their number has remained the same, indicating thereby that the pits are at the sites of emergency of dislocations. Thus the tests of match pattern and successive etch patterns successfully confirm that the etchant composed of 3part saturated solution of I_2 in methanol + 0 3 part HNo_3 (70%) + 0 3 part HCl (70%), is capable of revealing dislocations intersacting the cleavage surface.

Some other important observations on the etching results are as follows

Fig.16 shows etch grooves produced by the etchant. Also these etchgrooves have the etch pits at their terminations This configuration corresponds to the dislocation segment lying in the cleavage plane. The etch pit itself indicates the continuation of this dislocation into the crystal [23-24].

While carrying out the etching experiments the test specimen may get deformed if it is thin enough or the handling pressures are large. Plastic deformation caused due to these facts is usually accommodated by motion of dislocation. Fig.17 and 18 show the etch results which include such unintentional deformations. As observed in these photographs, the resulting dislocation motion is revealed by continuous etch trace with a point bottomed etch pit signifying the

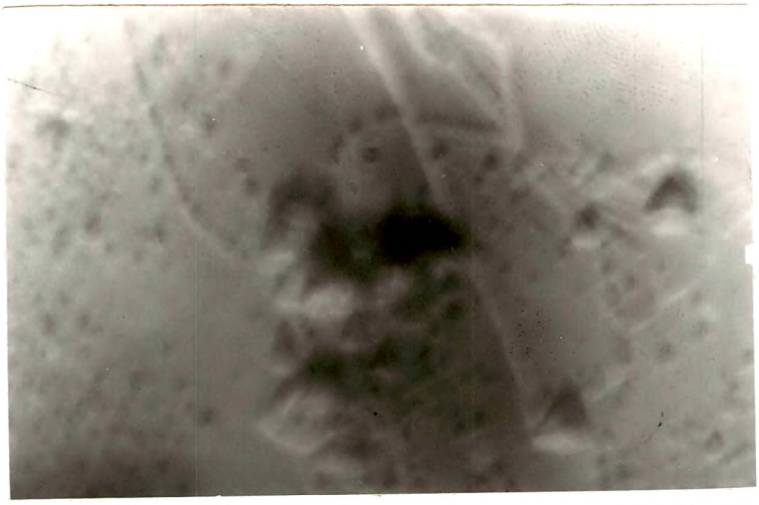

Fig.16 X 300

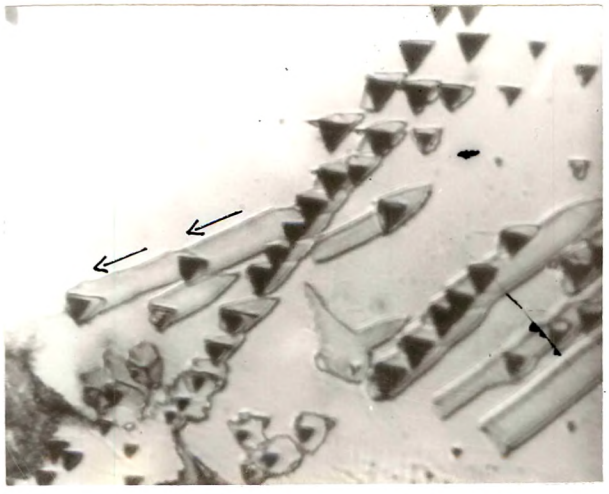

Fig.17 X 250

Fig.18 X150

final position of dislocation. The uniformity of the width of the trace indicates fast motion of dislocation [23 15]. One of the test samples was specifically bent while in the etchant. The dislocation motion is seen to be revealed by similar etch trace as shown in Fig. 19. The direction of the trace which is also the direction of dislocation motion is indicaed in the figures. All these examples (Fig. 17,18,19) the trace direction is the same, namely, perpendicular to the edge of the etch pit. This direction was found to be $[11\bar{2}]$. This is shown in Fig-19 where the direction $[1\bar{1}0]$, of the edge of the triangular pit is also shown for comparision.

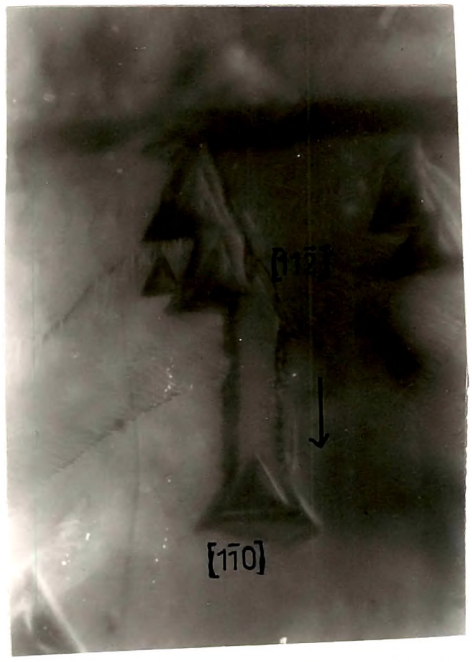

Fig 19 X400

Conclusions :

1. Fairly large, good quality crystals of $In_{0.1}Bi_{1.9}Te_3$, $In_{0.2}Bi_{1.8}Te_3$ and $In_{0.5}Bi_{1.5}Te_3$ can be obtained by zone melting method at the rate of 0.4 cm/hr and temperature gradient around 70°C/cm.
2. The crystal orientation at any In concentration, was observed to depend on the growth velocity. With increasing velocity the cleavage plane tends to orient parallel to the ingot axis.
3. The layer mechanism of growth is operative at low growth speed in the zone melting method.
4. As the growth velocity increases, the crystal perfection decreases.
5. As the number of zone passes increases the crystal quality improves i.e. dislocation density decreases.
6. The Bridgman method can also be used for growing these crystals.
7. The new dislocation etchant, 3part saturated solution of I_2 in methanol + 0.3 part HCl (70%) + 0.3 part HNO_3 (70%), is capable of revealing dislocations intersecting and lying in the cleavage plane. It also reveals dislocation motion.

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