PART - II

CHAPTER – 3

CRYSTAL GROWTH AND DISLOCATION ETCHING

CHAPTER – III

CRTSTAL GROWTH AND DISLOCATION ETCHING

Section – I

GROWTH

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

a) nature of material itself

b) its purity

c) thermal environment

d) the rate of growth

e) pressure

f) diffusion coefficients of the materials

g) impurity concentration and

h) homogeneity.

Crystals of a particular material can be grown by one or more of various techniques and the choice of a particular technique for growing crystal depends on the material properties and the purpose of application. Hence a systematic classification of growth techniques to simplify this problem has been given by Laudise[2]. There are three basic catagories of the crystal growth process :

1) Solid growth : S --- S Process involving solid phase Transitions.

2) Vapour growth : V --- S Processes involving gas-solid phase transitions.

3) Melt growth : L --- S Processes involving liquid-solid phase transitions.

TABLE – 1

APPLICATIONS OF SINGLE CRYSTALS IN VARIOUS TECHNOLOGIES

1. Cutting and Abrasives : Sapphire, diamond, SiC
2. Electroluminescent devices : GaP, GaAs, Ga(AsP)
3. Electromechanical transducers : Quartz, Rochelle Salt, ADP, CdS, GaAs
4. Filter and Oscillators : Quartz
5. Infra – red detectors : $Cd_x Hg_{1-x} Te$
6. Industrial bearings : Sapphire, Ruby
7. Lasers : $CaWO_4$, CaF_2, Yttrium – Aluminium Garnet, Ruby
8. Laser modulators, harmonic generators and Parametric devices : K.D.P., $LiNbO_3$ $LiTaO_3$, Barium Sodium Niobate
9. Microwave limiters and tunable filters : Yttrium – iron Garnet
10. Optical uses : CaF_2, Quartz, LiF, Calcite
11. Optoelectronic devices : GaAs
12. Radiation detectors : Anthracene, KCl, Si, GaAs, NaI doped with Tl, Ge doped with Li, Triglycine Sulphate, BaF_2. C_sF, CsI, BGO

13. Rectifiers : Si and Ge as the base materials

14. Semiconductors : Si, GaSb, InP, CdTe, (Pb,Sn) Te

15. Strain gauges : Si, Ga(AsP)

16. Thermoelectric devices and Electronic cooling system :$(Sb_x No_{1-x})_2Te_3$

17. Transistors : Si, Ge, GaAs as the base materials

18. Tunnel diodes, parametric diodes and Signal diodes : GaAs

19. Ultrasonic amplifiers : CdS

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

1. Crystal growth from solid state :

This method is rarely used and good quality crystals of large size cannot usually be obtained, except for certain metals where strain annealing is effective and also in certain cases where a crystal structure change occurs between the melting point and room temperature. The method of obtaining a crystal out of a polycrystalline ingot by strain annealing at high temperatures where stored energy of deformation serves as the driving force of recrystallization, is known as grain growth process.

2. Crystal growth from vapour phase :

This method is useful if the size of the crystal is not so important. But one can grow and obtain crystals with good perfection. This growth method bears its own theoretical importance and is useful to produce moderate size bulk crystals. The technique has been reviewed thoroughly by Holland, Kaldis, Schafer, Nitsche and Wickender et al[3-7]. This method is further divided into three categories.

a) Sublimation :

At a suitable high temperature, sublimation of the source material takes place. The sublimated material condenses into a crystalline solid by maintaining proper control over temperature and pressure conditions.

b) Vapour Transport :

The transport of the source material takes place as a volatile species by a suitable carrier gas to the crystallization region.

c) Gas phase reaction :

The growth of the crystals takes place as a product from the vapour phase, as a direct result of chemical reaction between the reactant vapour species. The method of crystal growth from vapour phase is rarely used to grow large crystals due to the problem of multinucleation. There are some exceptions such as CdS, ZnSe, GaP, GaAs and Cd_4GeS_6.

1. Crystal growth from aqueous solution :

This is the simplest and oldest method of growing crystals in which the material to be crystallized is dissolved in water or a suitable solvent to the desired degree of supersaturation. The solution is then slowly cooled or evaporated. Using a seed crystal and precise control over temperature, humidity and rate of evaporation, excellent quality large crystals can be grown. Well-known examples are ferroelectric and piezoelectric materials such as ADP, KDP, DGA and TGS. The limitation of this method for its application to other materials are the requirements of high solubility and chemical stability of solution.

2. Gel method :

The crystal growth from gel was first reported in 1913 by Leisegang, Bradford and Holmes. Substances having low solubility in water can be grown by gel method in which the constituent ions of the material slowly migrate through an inorganic or organic gel, react and form the compound. Hence the crystals grown by gel method are free from strain which is often present in the crystals prepared from melt or from vapour. During this growth, the crystal is nucleated due to the concentration of the compound which exceeds its solubility limit. This method is only used for research because of the obvious limitations of size. The crystals liked TGS, DGS, $KClO_4$ and many others have been grown successfully by this method. The method has been discussed in detail by Henisch[8].

5. Hydrothermal growth :

Crystals of many metals, their oxides and other compounds which are very less soluble or insoluble in water or which may be soluble in water only at high temperatures and high pressure are grown by this method. The requirement of high pressure is a practical difficulty in this method. The size and quality of the crystals obtained by this method are poor. The industrial production of commercial piezoelectric quartz crystals is an exception. The method has been discussed in detail by Ballman et al[9] and James et al[10].

3. High temperature solution growth :

This method is used for the solvents having high melting point, may be above 600°C. though this method basically involves practical difficulties of proper choice of solvent, chemical and phase stability of the solute and solvent, high melting point, obtaining high temperatures, contamination etc., many important materials are being grown by this method. Examples are YIG, lithium ferrite, gadolinium aluminate, barium titanate, $Ba_2MgGe_2O_7$, ruby, emerald etc. This method is applicable to almost any material for which a suitable solvent can be found and yields a perfection of crystals quite higher than that obtained by any other method. Also the crystals obtained by this method have usually higher concentration of impurities than that obtained by other methods. The optimum growth rate in this method is quite small. The principles and techniques involved in this method have been discussed by Elwell et al[11].

CRYSTAL GROWTH FROM MELT :

Crystal growth from melt is the most useful method due to the high growth rates obtainable. Numerous variants in this category exist and mainly involve the details of the geometry of the liquid – solid interface. The chances of impurity inclusion during the crystal growth from melt can be reduced with special efforts. Moreover, the crystal can be doped with a desired impurity to a desired concentration. Crystals of metals, metallic alloys, semiconductors, superconductors, ionic solids and alkali halides can be grown from melt. The method of crystal growth from melt has maximum theoretical importance since it is directly the process of phase change from liquid to solid involving systematic aggregation of atoms or molecules into crystalline order from their random distribution in liquid state of the same substance.

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

$$K_sG_s - K_LG_L = LV$$

where,

K_s = thermal conductivity of solid

K_L = thermal conductivity of liquid

G_s = temperature gradient in solid

G_L = temperature gradient in liquid

L = latent heat of fusion per unit volume

and V = growth velocity

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

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

(ii) Constitutional super-cooling.

The concept of constitutional super-cooling was introduced by Rutter et al[14]. The result of constitutional super cooling is the instability of the interface giving rise to cellular structure, dendritic structure, stray nucleation, waviness of interface etc., spoiling the quality of the crystal obtained. Further, Delves[13] has defined a parameter "S" known as constitutional super-cooling parameter given by,

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

Where G_{LS} = Solute concentration gradient in liquid

= $-V(C_L - C_S) / D$

V = growth speed

D = diffusivity of solute in liquid

C_L = concentration in liquid

C_S = required concentration in solid

m = slope of the liquids line at the given composition of alloy.

and G_L = temperature gradient in liquid

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

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

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

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

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

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

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

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

There are three basic techniques for crystal growth from melt :

(1) Bridgman method

(2) Czochralski method and

(3) Zone melting method

A short account of these methods is given below.

1. Bridgman Method :

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

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

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

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

(a) Metals[33-35]

(b) Semiconductors[36-37]

(c) Alkali and Alkaline earth haldies [38,39]

As per the specific requirements posed by the nature of materials, the technique has been developed into a sophisticated one. For example, Kamagawa et al[40] have grown $InSb_{1-x}Bi_x$ ($x < 0.03$) and $In_x\ Ga_{1-x}Sb$ ($x < 0.01$) ternary mixed crystals on InSb and GaSb seed crystals successfully by the Bridgman method with high speed rotation of about 80 to 120 r.p.m. Fang-Lang Hsu[41] has reported the growth of $(Sb_xBi_{1-x})_2\ Te_3$ single crystals with programmable temperature control by horizontal two zone Bridgman furnace in quartz ampoules evacuated to as low a pressure as 30x 10^{-7} torr. Voda et al[43] have grown pure and doped CdF_2 single crystals by the Bridgman method wherein unwanted vapour reactions were avoided by using an argon atmosphere and glassy carbon crucibles.

2. Czochralski Method :

A popular method of crystal growth from melt was developed by Czochralski[44] in 1918. This method is also known as Kyropoulos[45] method or the crystal pulling method. By this method the crystals with large size and relatively low dislocation density can be grown in a very short time. The main advantage of this method is that the size and diameter of the crystal can be controlled during the crystal growth process.

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

a) accurate control of temperature,
b) pulling rate and
c) rate of rotation

Here the diameter of the growing crystal depends on the temperature and the pulling rate but it is limited by the diameter of the crucible. The principles of the method have been discussed by Gilman[1] and Brice[30]. The practical aspects of this method have been discussed in detail by Draper[46]. The technique has reached hi-tech status due to its applicability for technologically important materials.

S r

Laudise et al[47] have grown doped single crystals of Bi_2Te_3 by Czochralski method in H_2 and in inert atmospheres. Wenzle et al[48] have grown copper crystals by Czochralski method in a hydrogen atmosphere at a pressure of 1 bar.

3. Zone Melting Method :

The zone melting method of crystal growth from melt was invented by Pfann[49] in 1952. In this method a small molten zone is created in a large solid ingot of the material to crystallize and is passed from one end of the ingot to the other end. The quality of the crystal depends on the relative zone length, growth velocity and the temperature gradient. The smaller the zone length, the better is the quality of the crystal .

Impurity removal :

The method which is capable of purifying a material to utmost sparse level of impurities by giving a large number of passes to the ingot in the same direction, is known as zone refining process. Here various impurities are collected at the two ends of the ingot (depending on their segregation coefficient). In this process, the impurities with segregation coefficients K >1, are collected at the farther end. The portion between the two ends of the ingot can be obtained purer after each successive zone pass.

Uniform doping of impurity :

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

Discontinuous bands of impurity such as in a p-n junction, are often required in the fabrication of semiconductor devices. This can be efficiently done by the zone melting technique. The theorectical and practical aspects of this method describing various modifications are discussed in detail by Parr[50] and Shah[51]. Herington[52] has reviewed the technique with particular reference to organic compounds. This method has been widely used to grow crystals and to refine various materials by different workers, e.g. Herman et al. Richards Delves, Hamaker et al, Brower et al and Swineheart [53-58]. The crystalslike InBi and Bi-Sb, have been grown in this laboratory using zone melting method by previous investigators (Bhatt et al and Shah et al)[59-61].

Balazyuk et al[62] have grown cadmium antimonide and zinc antimonide single crystals by the zone melting method to study the effect of crystal growth condition on the structural perfection and thermal properties. Lunin et al[63] have studied the distribution of AlSb in varizone layers of Al_xGa_{1-x} Sb growing in a temperature gradient field. Shukla et al[64] have grown $CdBr_2$ single crystals by the zone melting method. Serra et al[65] have successfully grown large area zinc sheet single crystals by using a modified zone melting method. This is a hybrid of the zone melting and the horizontal Bridgman techniques. Fan Zhanguo et al[66] have used the zone melting method for preparing YBaCuO superconductor successfully.

Lostak et al[67] have grown $Bi_{2-x}In_xSe_3$ (x = 0.00 to 0.66) single crystals using a modified Bridgman method. The crystal homogeneity was studied by determining the indium content and the variations of Seeback coefficient in the directions perpendicular and parallel to the crystal axis. Subramanian et al[68] have grown ternary mixed $InBi_2Te_4$ crystals and obtained semiconducting polycrystalline ingots. Jansa et al[69] have successfully grown $Bi_{2-x}In_xTe_3$ crystals (x = 0.1) by Bridgman method.

Sagar et al[70] have grown Bi_2Te_3 crystals by Bridgeman method and Arivoulli et al[71] have grown Bi_2Te_3 crystals by vapour phase technique. Kutasov et al[72] have grown $Bi_2Te_{2.8}Se_{0.2}$ crystals by .
Loudise et al [73] have grown doped single crystals of Bi_2Te_3 by Czocharlski method in H_2.

Single crystal of Bi, Cd, Sb, Se, Te, Zn, Bi-Sb, Se-Te, In–Bi, SnSe, and $SnSe_2$ have been growth from melt by Bridgman, Czochralski, zone melting and Chalmers methods by various workers (Bhatt et al, Bhatt, Balasubramaniam, Thattey, Shah B. S., Thakar, Vaishampayan, Pandya, Vyas, Trivedi M.D., Trivedi S. B., Shah R. C. and Gireesan) [74-86].

There is no report of growth studies on $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals. The present study is mainly concentrated on

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the Bridgman method. However, Zonemelting method is also used and results are reported.

Crystal Growth of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$:

Antimony, selenium, tin, bismuth and tellurium each of 5N purity were purchased from Nuclear Fuel Complex, Hyderabad, India. The stoichiometric amounts of all the materials were weighed accurately upto 10 micrograms using a semimicrobalance and filled in the quartz ampoule of about 10 cm length and 1 cm diameter. The quartz tube was then vacuum sealed at the pressure of about 10^{-4} Pa (in order to prevent oxidation of material) and it was kept in the alloy mixing furnace (Chapter 2). In this mixing unit, the material was mixed in the molten state for about 48 hours by rotating the tube at 10 r.p.m. at 635°C temperature. The rotation of the tube was then stopped and the material was further kept in the molten state for another 24 hours in order to ensure homogenization and complete reaction in the the molten charge. It was then slowly cooled to room temperature. This process usually produces fairly homogeneous compound.

The temperature was measured and controlled with a proportional temperature controller within ±5 °C using Chromel-Alumel thermocouple. For crystal growth by the Bridgman method,the ampoule with the ingot was kept in the vertical Bridgman furnace . The length of the core of the furnace was about 45 cm. A baffle was kept at 23 cm.i.e. between the two halves of the furnace. The inner diameter of the core was 5 cm. The upper furnace was kept at 630 °C i.e. ~ 65 °C higher than the melting point and the lower furnace was set to various temperatures below melting point to obtain various gradients. A typical temperature profile of the double furnace is shown in Figure 1 together with the starting position of the ampoule. The ampoule was kept steady for 24 hours in the upper hot zone of the furnace and was solidified at different lowering rates in the range of 3.5 mm/hr to 12 mm/hr and temperature gradients about 45°C/cm. The crystals obtained were about 4 cm in length and 1cm in diameter. They could be cleaved easily. Microscopically the cleavage plane of the crystal was found to be fairly planar. The cleavage plane is (111) in all the three cases.

A number of crystals of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ were grown by the Bridgman method under the gradient of 45 ° C/cm at different growth velocities and the average dislocation density in each case was determined (Table – 2).For this purpose, the chemical dislocation etchant discussed in the next section was applied on the cleavage surfaces from different parts of the crystal ingot and the etch-pit count method was used. It can be seen from the table that the crystals obtained at different growth velocities are of good general perfection with dislocation density of

Fig. 1

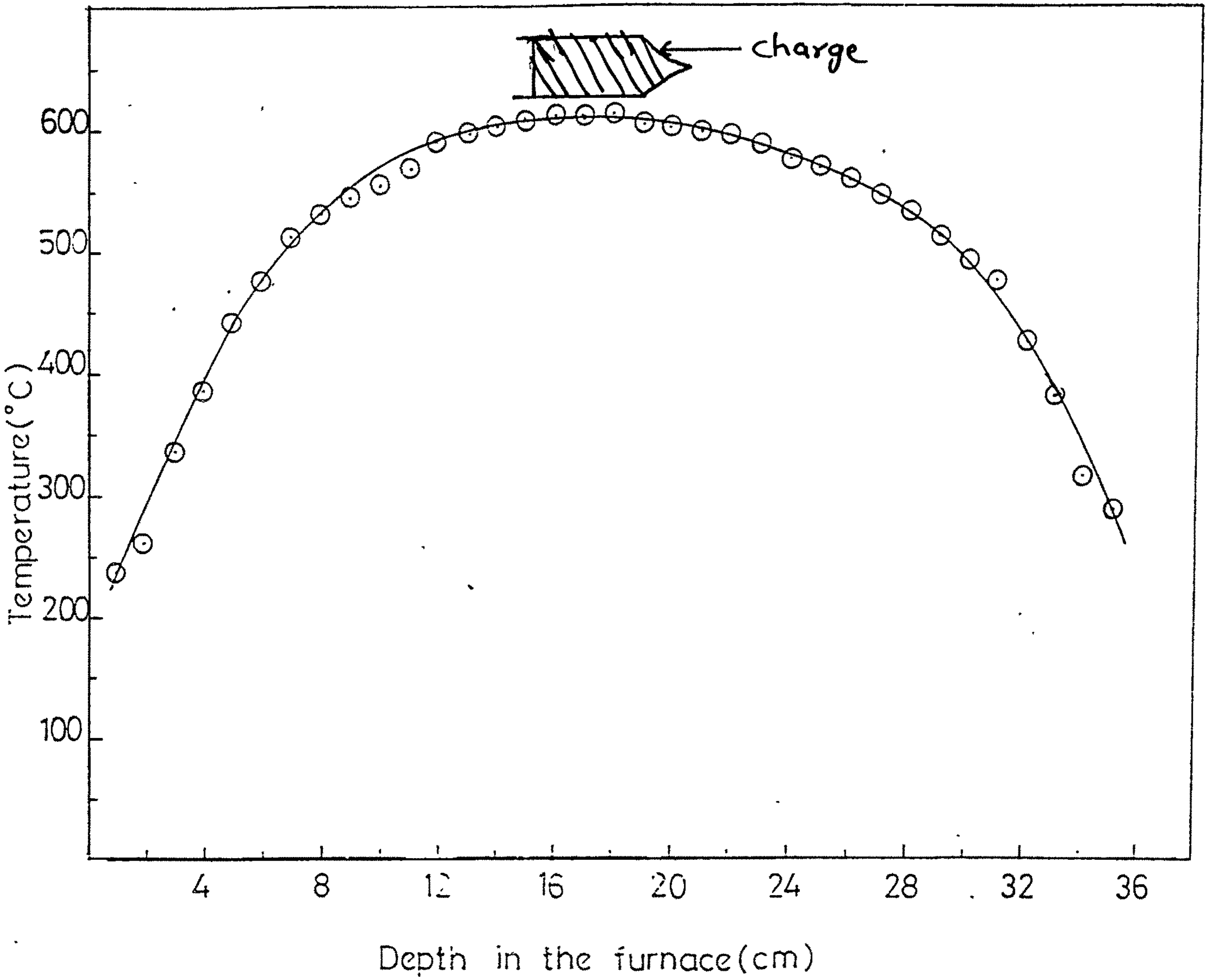

charge
Temperature(°C)
600
500
400
300
200
100
4
8
12
16
20
24
28
32
36
Depth in the furnace(cm)

Table : 2

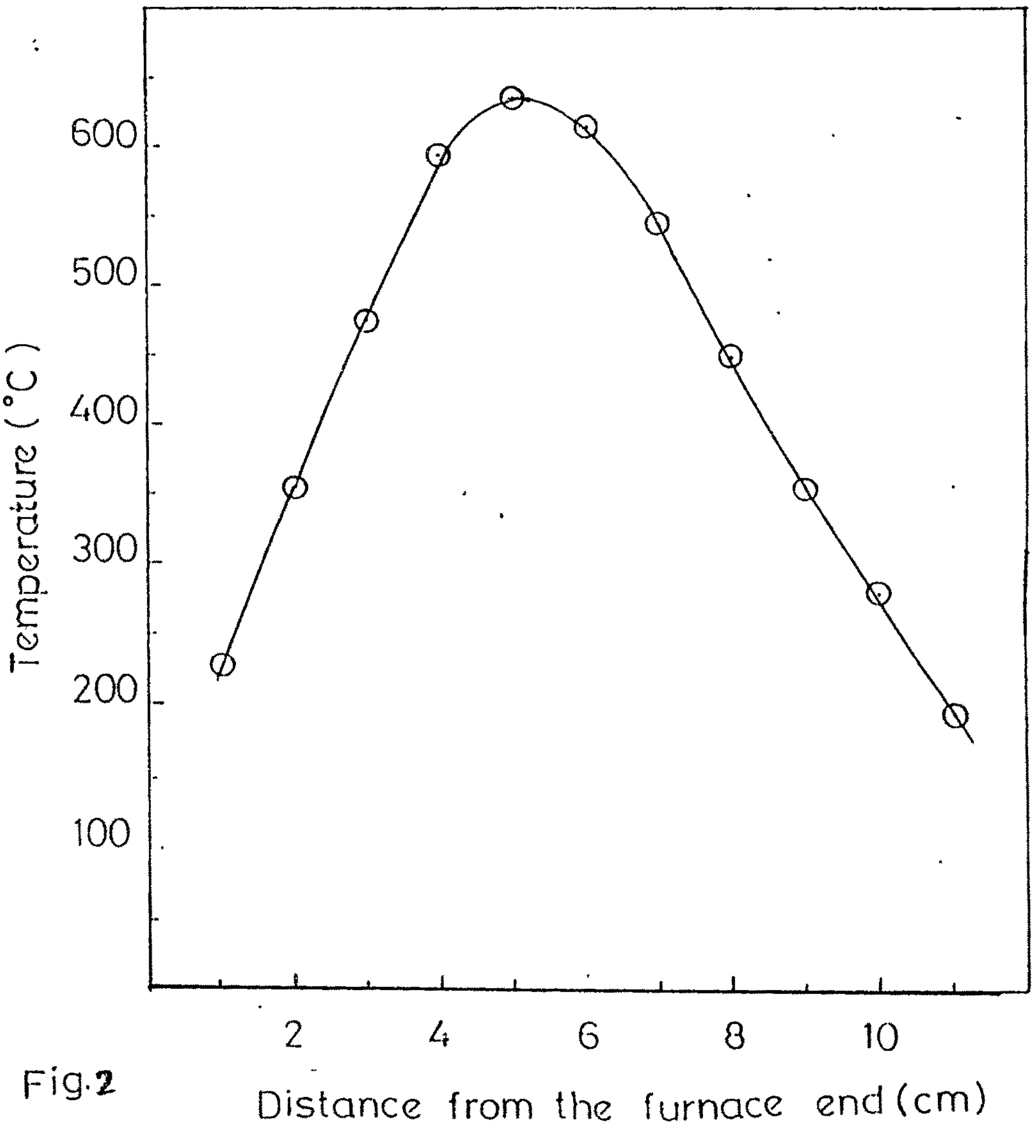
Variation of dislocation density with growth velocity

Crystals	Growth velocity Cm/hr	Number of crystals grown	Average dislocation density cm^{-2}
$Sb_{0.2}Bi_{1.8}Te_3$	0.35 0.70 1.20	5 3 3	1.9×10^5 2.1×10^5 2.5×10^5
$Sn_{0.2}Bi_{1.8}Te_3$	0.35 0.70 1.20	5 3 3	1.7×10^5 1.8×10^5 1.9×10^5
$Bi_2Te_{2.8}Se_{0.2}$	0.35 0.70 1.20	5 3 3	1.8×10^5 2.1×10^5 2.4×10^5

the order of 10^5 cm^{-2}. However, the dislocation density does show a systematic dependence on growth velocity, viz, it increases with growth velocity. At the growth velocity 0.4 cm/hr, the average dislocation density was found the least among all the crystals.

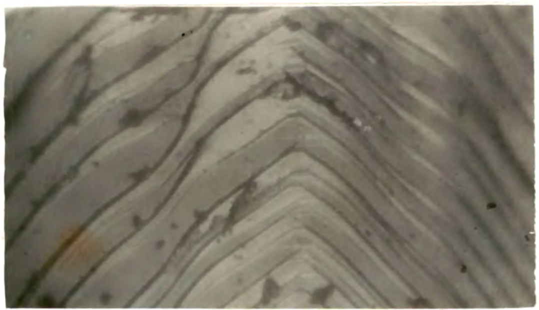
The $Sb_{0.2}Bi_{1.8}Te_3$ compound prepared as discussed above was also used for growing single crystals by zone melting method. The starting ingot was about 7 cm in length and 0.8 to 1 cm in diameter. The temperature profile of the zone-furnace is shown in Figure-2. First the ingot was zone levelled. The temperature gradient across the two solid-liquid interfaces was about 90°Ccm^{-1} giving a zone length of about 8 to 10 mm with maximum temperature 630 °C. To level off impurities, 30 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 velocities ranging from 0.35 cm hr^{-1} to 1.2 cm hr^{-1} were used.

The crystals of $Sb_{0.2}Bi_{1.8}Te_3$ obtained by zone melting method were found to exhibit some well-defined growth features on the free surface. Figures-6 and 7 show these features. Figure –6 shows layers spreading over the surface of the crystal, indicating the layer mechanism to be effective.



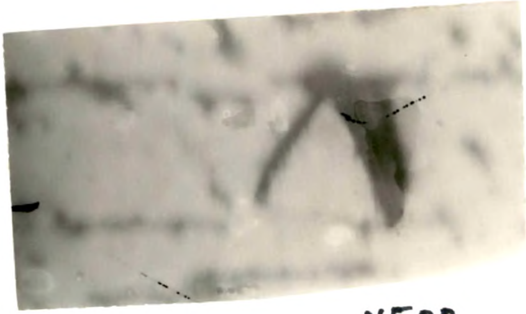
600
500
400
300
200
100
Temperature (°C)
2
4
6
8
10
Distance from the furnace end (cm)

Fig.2



X 400

Fig. 6



X500

Fig. 7

Figure –7 displays an interesting feature. The triangular feature observed is in elevation with respect to the other surface area as implied by the focussing difference observed under microscope . In the photograph also the triangle is well-focused as compared to the surrounding region. These facts indicate the feature to be a distinct hillock formed on the surface. The three fold symmetry of the hillock is in conformity with the crystal symmetry. Such hillocks were quite frequently observed and they would indicate the (111) oriented growth of the observed surface. This is typical of the layer growth mechanism[87]. An example of multinucleation of hillocks is illustrated in Figure-8.

In metals, alloys or intermetallic compound crystal growth, striated structures are not an unusual phenomena. An example of well-defined rectilinear striations observed on the top free surface of an as-grown crystal is shown in Figure –9. The appearance of these features was found to be practically independent of the growth velocity. The striations observed by Marizone et al[88] in their studies on InSb crystals have been interpreted as impurity striations. Further they have shown that these striations are related neither to the type and amount of impurity nor to the orientation and growth rate,but are rather dependent on the convection currents in the melt. Whereas, the striations observed by Teghtsoonian et al[89] in the case of

X400

Fig.8

X500

Fig.9

InSb single crystals have been shown to be associated with cellular structure of the solid- liquid interface. The striations observed in the present case may be due to unintentional impurity which may for example be oxides formed on the surface or due to convection currents.

It is known that while using the zone melting method of crystal growth, the technique of zone levelling is very effective in producing uniform distribution of impurity. As a result of the uniform impurity distribution, the zone levelling also improves the crystal perfection. This is because the difference 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[90]. A sufficient experimental evidence in this respect has been reported as long back as 1956 (Goss et al and Pfann [91-92]. Thus since number of zone passes affects homogeneity and hence the perfection of crystals, at least two crystals were grown with large number of alternate zone levelling passes, namely;10, 20 and 30. For these growths, the growth velocity was kept constant, namely 3.5 cm hr^{-1}. Table -3 gives the measured average dislocation density of the crystals. Remarkably, increasing the number of zone passes from 10 to 30 has decreased the dislocation density.

Table – 3

Variation of dislocation density with number of zone passes

Numer of zone passes given in alternate directions	No.of Crystal grown	Dislocation density cm^{-2}
10	2	1.9×10^5
20	2	1.6×10^5
30	3	1.2×10^5

For X-ray diffraction characterization, powdered samples from different parts of the crystal were used to obtain X-ray diffractograms. The x-ray diffractometer, Philips PM 8203 with pw 1390 channel control and pw 1373 goniometer was used. It was operated at 35 to 40 KV and 20 mA with Cu target (λ = 1.5418 Å). The typical diffractograms of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals are shown in Figure – 3,4 and 5, respectively. The patterns consist of well- defined sharp diffraction lines indicating good crystallinity of the specimens. The identifaction of the peaks in diffraction intensity was made using JCPDS data card [93]. The compound and index assignments are indicated on the major peaks in the respective plots. The observed and the JCPDS file d-values are found to be in a fair agreement. Bi_2Te_3 has a rhombohedral structure and its hexagonal unit cell is often used for crystal structure studies[70]. Y.Feutelais et al.[94] have reported the values of lattice parameters of the hexagonal cell, a=4.395 Å and c= 30.44 Å, in good agreement with our calculated parameters: a= 4.387 Å, 4.371 Å and 4.381 Å and c= 30.39 Å ,30.34 Å and 30.41Å, respectively of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ crystals.

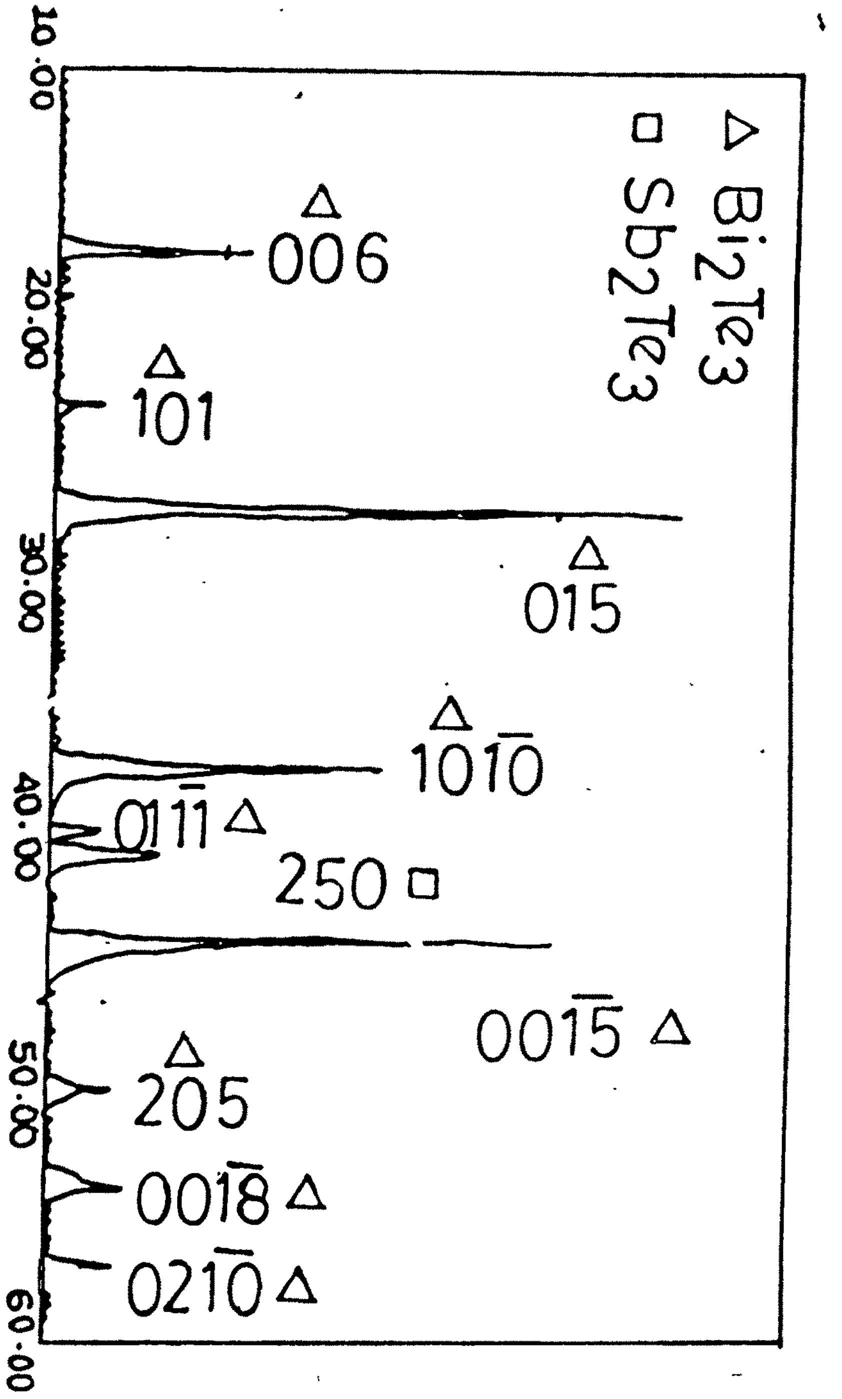
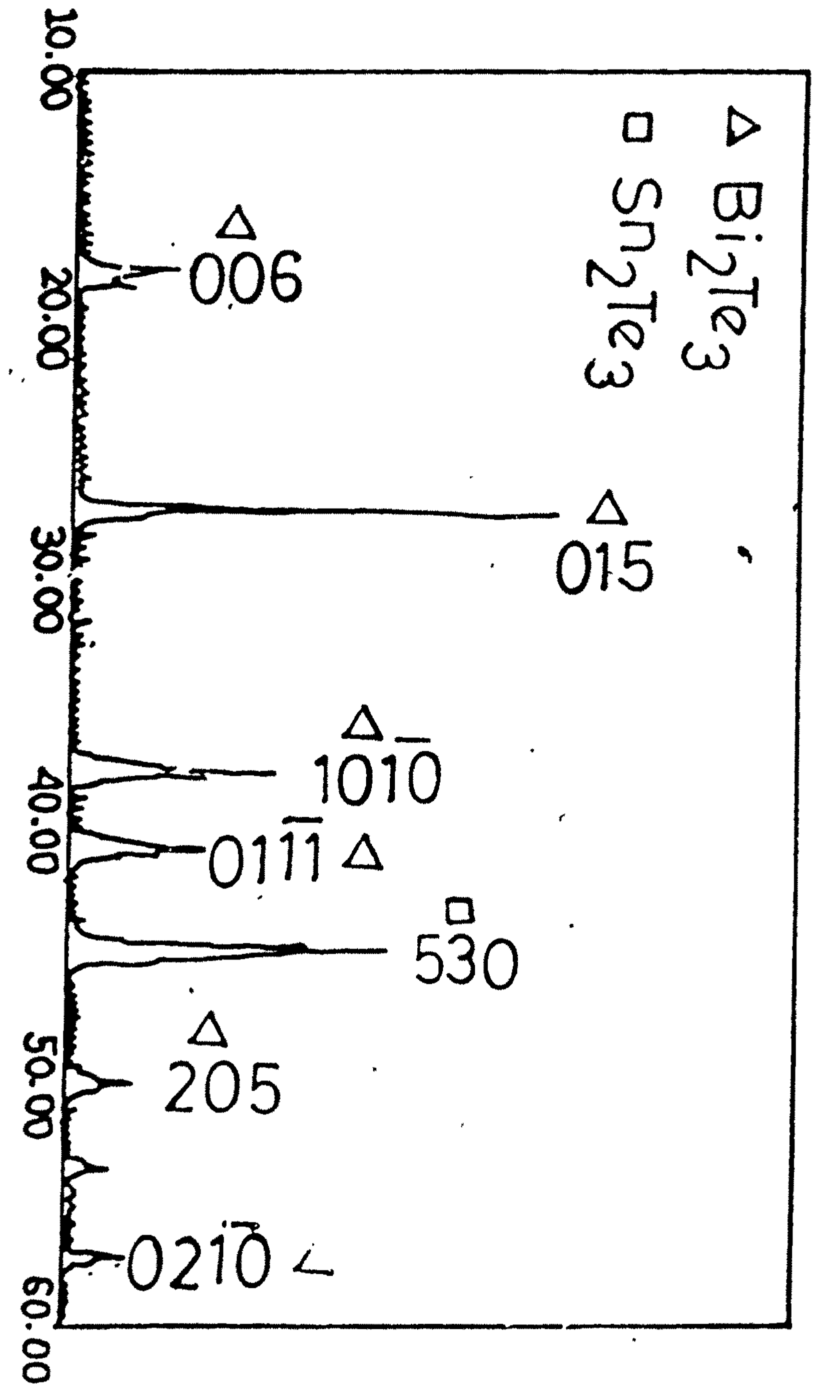

△ Bi_2Te_3
□ Sb_2Te_3
10.00
20.00
30.00
40.00
50.00
60.00
006 △
101 △
015 △
$10\overline{10}$ △
$01\overline{11}$ △
250 □
$00\overline{15}$ △
205 △
$00\overline{18}$ △
$02\overline{10}$ △

Fig. 3



10.00
20.00
30.00
40.00
50.00
60.00
Δ Bi_2Te_3
□ Sn_2Te_3
Δ 006
Δ 015
Δ 10$\overline{10}$
01$\overline{11}$ Δ
□ 530
Δ 205
02$\overline{10}$ Δ

Fig. 4

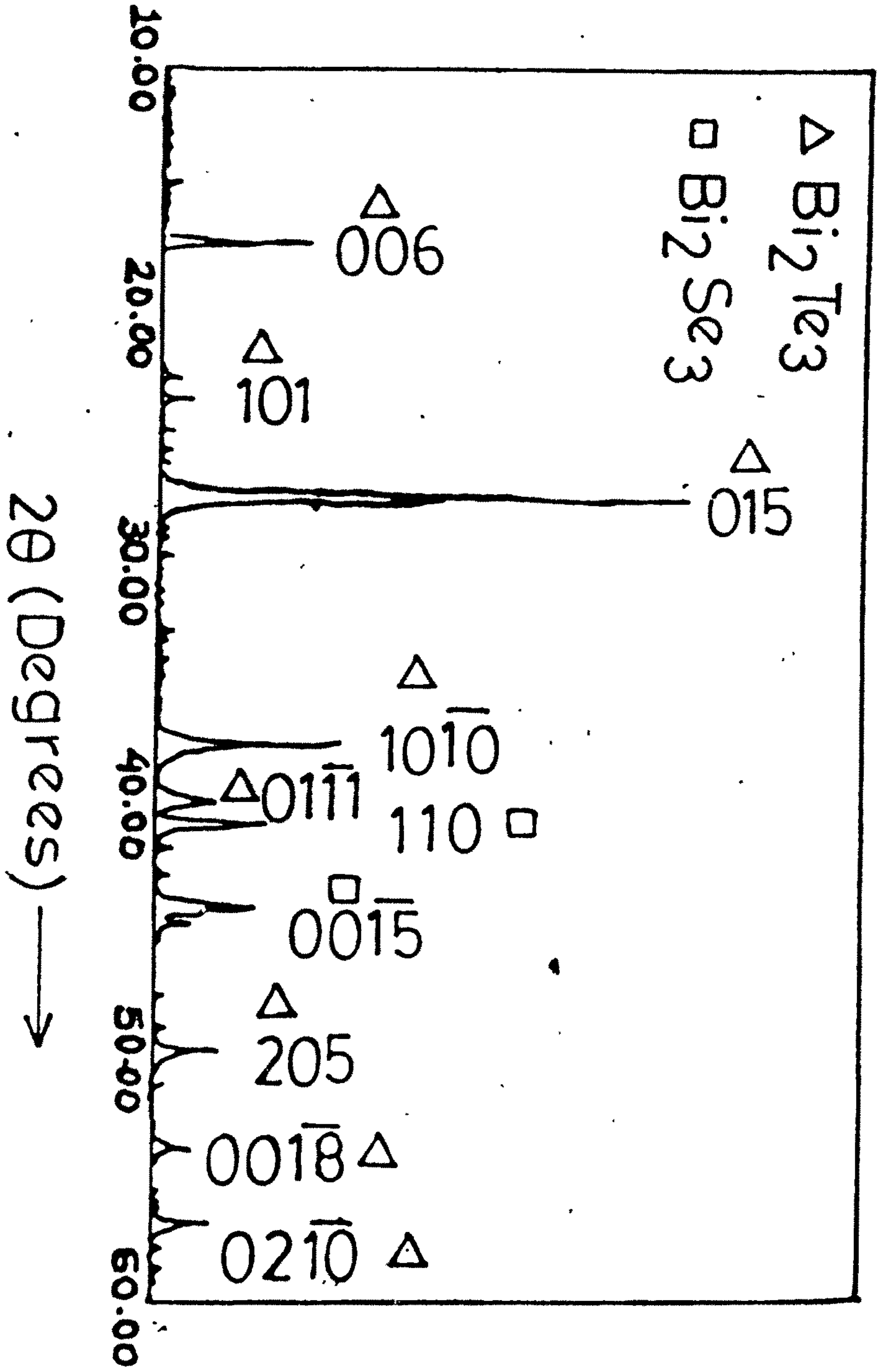

△ Bi_2Te_3
□ Bi_2Se_3
10.00
20.00
30.00
40.00
50.00
60.00
2θ (Degrees)
△ 006
△ 101
△ 015
△ $10\overline{10}$
△ $01\overline{11}$
110 □
□ $00\overline{15}$
△ 205
$00\overline{18}$ △
$02\overline{10}$ △

Fig. 5

SECTION – II

DISLOCATION ETCHING

All real crystals contain defects. Various important properties of a crystal, from electrical conductivity to hardness, depend to more or less extent on these defects also. There are various types of defects in a crystal :

1. Point defect
2. Line defect
3. Planar defect and
4. Volume defect

The line defect is of two types, edge and screw dislocations [95]. It affects most of the physical properties of a crystal to a significant extent according to Orowan[96], Polanyi[97] and Taylor[98].

The dislocation in as grown crystal may originate due to

1. propagation from seed crystal
2. shear strain due to mechanical and thermal stresses
3. dendritic growth
4. collapse of vacancies[99]

The properties of dislocations with their various geometrical features have been well-worked out [100 - 102]. Crystal perfection can be judged in terms of its dislocation content, through many other lattice imperfections exist in a crystal. The dislocation density is defined as the dislocation line length per unit volume. The other practical definition used to measure dislocation density is, the number of dislocations inter-secting a unit area of a surface of the crystal. Mott et al [103] and Frank [104] proposed that dislocation lines can be curved and assume any orientation. Though dislocations may exist in the form of closed loops inside the crystal and hence don't intersect any surface of the crystal, this definition has been used as a fairly good measure of dislocation density. Various methods are employed to study line defects (dislocations), some of them being direct and other indirect. Electron microscopy and x-ray diffraction belong to the first class. Some times, the crystal is decorated by "suitable coloured impurity" provided it is transparent.

The simplest and easily accessible technique employed to observe dislocations is the "etch-pit" technique [105-107]. The etch pits at the sites of dislocations can be formed either by chemical reaction or by physical dissolution of a crystal in a suitable solvent known as an etchant. Some times, etching is also done by other methods like ion bombardment or by thermal treatment. The etching process is in general al most opposite to that of growth.[108-110]

Three dimensional dislocation structures can be made visible by the method known as decoration. In this method, suitable chosen impurity is allowed to precipitate along dislocation lines which makes the dislocations visible under the microscope in optically or infrared transparent crystals. Dislocations were observed by this method in silicon crystals by Dash[111], in Silver halides by hedges et al[112] and in Alkali halides by Amelinckx[113].

The chemical dislocation etching technique is discussed below in detail with the discussion limited to metals and semiconductors and wherever it is necessary, some references to non-metals are given. The chemical etching gives rise to various types of geometrical features on a crystal surface. Due to anisotropy of a crystal, the dissolution / reaction rates are different in different directions giving rise to the production of depressions, with regular geometrical out lines at the preferential sites of attack on the crystal surface, known as etch pits, etch marks or etch figures. The form and symmetry of such etch pits were used by minerologists to determine crystal planes and their orientations. Dissolution of a crystal surface is effected by the retreat of monomolecular steps, the process being reverse to that of growth which takes place due to the addition of steps on the surface. It is believed that when a crystal face is exposed to a solvent, dissolution begins by nucleation of unit pits of one molecule depth and these unit pits grow as steps retreat across the crystal surface through the action of kinks. The chemical etching of a crystal surface involves the following sequence :

Reactants :

1. Approach the surface
2. Interact with the surface and
3. React chemically

Products

1. Disengage themselves from the surface
2. Move away from the surface

Gatos[114] and Gatos et al[115] reported that the overall etching process may be electrochemically controlled or diffusion controlled or controlled by a combination of both. The factors affecting the process of dissolution of a crystal surface are as follows :

a. Crystallogaphic orientation of the surface
b. Impurity concentration on the surface
c. Crystal defects present in the surface
d. Surface damage and cleanliness.

The above said factors affecting the etching process are discussed in detail by Irving[116]. Regarding the formation of etch pits at dislocation sites, explanations have been given by various workers. For the initiation of etch pits, the presence of impurities preferentially segregated at dislocations was considered essential for long time. Impurity segregation has been reported to be responsible for the formation of dislocation pits in zinc and copper crystals[117-118].

1. Cabrera[119] and Gilman et al[120] have reported the etch pit formation as nucleation process analogous to crystal growth and attributed the nucleation of etch pits to the elastic energy associated with dislocations. A new approach to the problem was given by Frank[108] proposing a kinetic theory of growth and disslotion. The theory was later applied to etching process[121]. According to this, the visibility of an etch pit depends on

a. The dissolution velocity V_b, along the dislocation line,

b. The ledge dissolution velocity V_l and

c. The average vertical dissolution velocity V_s, at a dislocation free region of the crystal surface.

For the formation of visible etch pits,

$$V_d / V_l \geq 0.1 \; V_d > V_s$$

An excellent review of etching as used on LiF crystals has been given in detail by Gilman[122]. The technique has also been used to study dislocations in some present day important crystals like $Cd_xZn_{1-x}Te$ and CdTe.[123-124] The formation of slip pattern in copper crystals and its dilute alloy crystals has been very fruitfully studied by etching[125].

In order to study the etching mechanism with various parameters, systemetic investigation has been carried out by many workers.[126-131] Lin et al[132] have reported anisotropic etching on different crystallographic surfaces of AlSb single crystals. To study dislocations, in some cases, the chemical etching is done in magnetic field [133-134] or electric field.[129] Also a crystal can be etched electrolytically.[135 - 136]

The reliability of an etchant as a dislocation etchant can be judged by one or more of the following tests :

1. Etch pits associated with individual dislocations reappear after each successive polishing and etching, since a dislocation line cannot terminate inside a crystals.
2. The etch pattern produced by the etchant on two oppositely matched cleaved surfaces should appear as mirror images of each other, if cleavage of a grown crystal is possible. Sagar et al[137] and Bhatt et al[138] have shown branching and bending of dislocations at the cleavage which may result in deviations from one to one correspondence of etch pits on the oppositely matched cleavage surfaces.
3. The etch pit density should show a reasonable agreement with the theoretically estimated dislocation density.
4. Plastic deformation always involves the creation and motion of

dislocations which result in increase of etch pit density at least in the vicinity of the region of deformation.

For the development of a dislocation etchant for a given material, a trial and error method has usually to be used. Etching can be efficiently used to characterize the crystal and [139-146]

1. To decide whether a given solid is a single crystal or not.
2. To distinguish between different faces of a crystal.
3. To reveal the growth history of a crystal.
4. To determine dislocation density of a crystal.
5. To assess the impurity distribution.
6. To study stress-velocity relation for individual dislocation motion.
7. To study deformation patterns like pile-up and polygonization.
8. To study dislocation multiplication.
9. To study plastic flow around indentation.
10. To study fracture mechanism.
11. To study slip and twin systems and interaction of dislocations under stress.
12. To study kink configuration and inclination of

dislocation.

13. To study origin of dislocations in as grown crystals.

14. To distinguish between fresh and as-grown dislocations.

15. To delineate grain boundary and

16. To study polarity of crystal lattice.

Thus chemical etching, though an old technique is quite useful even in modern days in a variety of crystals.[87,147-155] The results of dislocation etching on their cleavage faces carried out by the author are discussed below.

DISLOCATION ETCHING OF CRYSTLS

The crystals grown as described in section-I were cleaved at 0°C. The constant orientation of the cleaved plane along the entire length of the ingot indicated the sample to be necessarily a single crystal. We have found no misorientation on the cleavage plane as observed under optical microscope. This observation is also supported by our etching studies. The crystals were free of grain boundaries except for occasional low angle boundaries.

Sagar et. Al, have reported chemical etching of Bi_2Te_3 single crystals[70]. Their results were found difficult to reproduced, which may be due to the presence of Sb,Sn and Se in the present case. However, the author after numerous trials has developed a dislocation etchant to work on the (111) surfaces of these crystals. The various trials and their results are outlined below in Table 4. As can be seen in the table the most suitable etchant consists of 3 part conc. solution of iodine in methanol, 0.3 part HCl (70%) and 0.3 part HNO_3 (70%). This mixture was used to etch the surface of freshly cleaved crystals. The minimum etching time to produce well-defined triangular etch pits at room temperature was about 30 sec. and this could be extended to 60 sec. without deteriorating the surface to any appreciable extent. The etching was followed by rinsing the etched sample in methanol and air-drying.

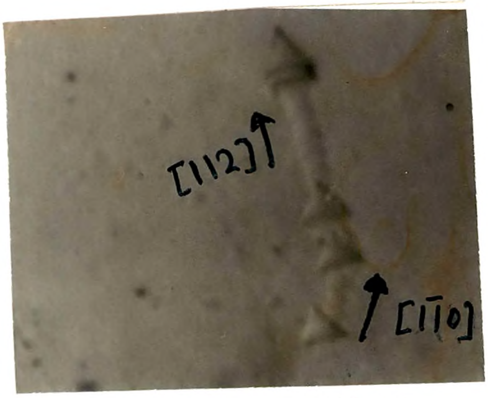
Figure 10 shows the etch-pits developed in 30 sec by this etchant on the as-cleaved surface of a $Sb_{0.2}Bi_{1.8}Te_3$ crystal. It can be seen that the etch-pits are point bottomed and have regular triangular outlines. They also have the same orientation. Such etch-pits along the surface reassert the specimen to be a single crystal. The 3 – fold symmetry of the pits is consistent with the 3-fold axis perpendicular to the observation plane which is (111). Figure 11 illustrates an interesting etch-groove pattern obtained. It is important to note that the groove is terminated by etch-pits. Such etch–grooves were found to be along definite directions. The directions analysed using stereographic analysis[156] were found to be [112] and $[1\bar{1}0]$ as indicated on the

TABLE – 4
EFFECT OF ETCHANT COMPOSITION ON ETCHING CHARACTERISTICS :

Sr. No.	Etchant	Etching time sec.	Etching charateristics
1.	1 part conc. solution of iodine in methanol + 0.5 part H_2SO_4	20	surface spoiled
2.	1 part conc. solution of CrO_3 in water	10	film deposit on surface.
3.	1 part HNO_3+ 1 part HCL+ 1 part H_2O	60	surface was spoiled
4.	4 part HNO_3+ 2.5 HCl + 2.5 H_2O	30	irregular shape of pits, corrosion.
5.	5 part conc. solution of iodine in methanol + 1 part HNO_3	20	equilateral triangular pits most of them flat bottomed size varying.
6.	14 part conc. solution of iodine in methanol + 1 part HNO_3	30	equilateral triangular pits most of them flat bottomed size varying.
7.	14 part conc. solution of iodine in methanol + 1 part HNO_3	15	equilateral triangular pits most of them flat bottomed, very small size.
8.	7 part conc. solution of iodine in methanol + 0.5 part HNO_3	60	equilateral triangular pits most of them point bottomed, but little corrosion observed.
9.	3 part conc. solution of iodine in methanol + 0.4 part HCl+ 0.2 part HNO_3	25	equilateral triangular pits, most of them point bottomed size varying.
10.	3 part conc. solution of iodine in methonol+ 0.3 part HCl+ 0.3 part HNO_3	30	point bottom triangular etch-pits of nearly uniform size.

×600

Fig. 10

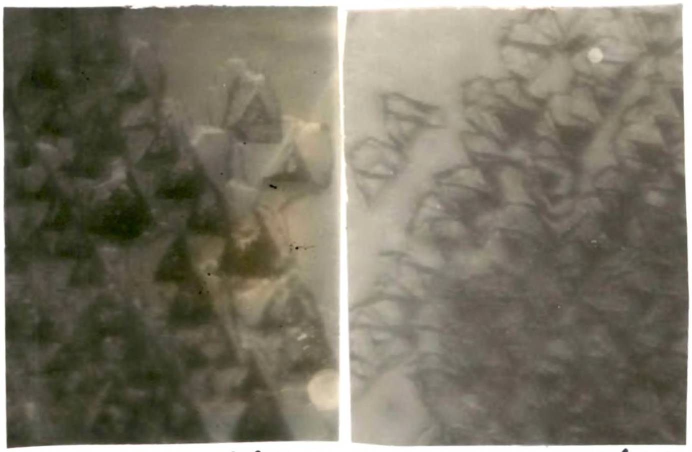


×700

Fig. 11

photograph. The etch-grooves produced by a dislocation etchant are known to correspond to dislocations parallel to the surface rather than inclined to it[157]. Not frequently observed, such pattern indicates a dislocation pair intersecting the observed plane and connected by a dislocation lying in the surface. In the cited example, the surface confined dislocations are along [112] and $[1\bar{1}0]$ directions delineated by the etch grooves.

Matching of etch-pits on oppositely cleaved crystal faces is a good test of dislocation etchant. Etch patterns obtained on oppositely matched cleavage faces are shown in Figure 12. It can be seen that there is almost one to one correspondence of etch pits observed, implying that the etch pits are necessarily at dislocation sites. Figure 13 illustrates etch grooves obtained after etching the specimen for 30 sec. Thus, apart from isolated dislocations, low angle boundaries are also seen delineated by the etchant. Further tests for dislocation etchant, like successive etching of a surface, scratching or indenting the surface and etching it, were conducted to yield satisfactory results. Thus, the etchant composition stated above is capable of revealing the grown-in and freshly produced dislocations intersecting the cleavage plane.



X650 x600

Fig. 12

x500

Fig. 13

CONCLUSIONS :

1. Fairly large good quality crystals of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ can be obtained by the Bridgman - Stockbarger technique at the ampoule lowering rate of 3.5 mm / hr. and temperature gradient around 45°C /cm
2. In the case of $Sb_{0.2}Bi_{1.8}Te_3$, single crystals can be obtained by Zone melting method and the observation on growth features indicates the layer mechanism to be effective in the growth of the crystal.
3. As the growth velocity increases the crystal perfection of $Sb_{0.2}Bi_{1.8}Te_3$, $Sn_{0.2}Bi_{1.8}Te_3$ and $Bi_2Te_{2.8}Se_{0.2}$ decreases. The dislocation densities are found to be in the range of 10^5 cm^{-2} in the crystals grown under the above stated conditions.
4. The new chemical etchant: 3 part conc. solution of iodine in methanol, 0.3 part HCl (70%) and 0.3 part HNO_3 (70%) is capable of revealing dislocations intersecting the cleavage plane and also lying along it.

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