CHAPTER – 7

CHEMICAL ETCHING OF $InBi_{1-x}Sb_x$ AND $InBi_{1-x}Se_x$

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The work carried out and reported in this chapter deals with the results from the chemical etching work on the cleavage planes of $InBi_{1-x}$ Se_x / Sb_x single crystals. No systematic study on chemical etching of these single crystals has so far been reported. Two dislocation etchants for both these single crystals are developed by the author. The results obtained with these new dislocation etchants are discussed. The etchants developed have been used to assess the perfection of crystals and in the study of deformation of these crystals.

For reveling dislocations, chemical etching is the simplest method. The selective nature of the etching phenomenon is influenced by a number of factors like, the nature of the individual crystals, crystalline perfection, crystallographic orientation, type and concentration of impurities in the crystals as well as in the etchant, the temperature and the hydrodynamics of the solid-liquid interface. Chemical etching has a wide range of applications and is used:

1. For revealing defects in the crystalline materials, to study the behavior and mode of formation of dislocations.
2. For orientation determination in conjunction with optical goniometry.

3. For preparation of clean surfaces.
4. To obtain reproducible electrical properties of semiconductors.
5. To determine the nature of impurity distribution and
6. For controlled removal of materials

The discussion which follows is confined to the use of chemical etching for studying crystalline defects (dislocations in particular) only.

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 revealing dislocations which makes it a valuable tool for studying perfection and plasticity of crystalline materials. Etching methods have been successfully developed for various single crystals namely Germanium(1), Silicon(2,3), Silicon – Iron(4), Zinc(5), Lithium Flouride(6), Silicon carbide(7), Copper aluminum alloys(8), $BiSb_{(2-y)}Te_xSe_{(3-x)}$(9) and Bismuth telluride(10) etc. to mention only a few. Typically etching has been used on {511} planes to evidence the polar structure of CdTe crystals (Iwanaga et al)(11). Dislocation etching can be very fruitfully used to test the crystal perfection and slip deformation under the effect of as low an impurity concentration as 0.05 at % (Imashimizu et al)(12).

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

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

Various workers have reported etchants for InBi single crystals. Roy et al[13] and Walter[14] have reported a few dislocation etchants and shown that the results were quite difficult to be reproduced and frequently the etch pits were of irregular shape. Bhatt et al[15] have also developed a dislocation etchant consisting of 1 part "A" and 10 parts of glacial acetic acid. Where "A" is 10 parts 0.05M CrO_3 and 1 part HNO_3 (70%). They obtained well defined point bottomed square pits, exhibiting the four fold symmetry of the (001) cleavage plane and further observed that this etchant was capable of revealing dislocations intersecting the cleavage plane. They have also used this etchant to measure the average dislocation density of InBi single crystals and to study plastic deformation and fracture mechanisms in InBi single crystals.

A systematic study of the development of an etchant for $InBi_{1-x}$ Sb_x / Se_x crystals was undertaken by the author and the results are compared. In attributing the etch pits to dislocations the following criteria were adopted:

1. Matching of etch pits on cleavage counter parts should be reasonably good.
2. Etch pit density (i.e. dislocation density) should remain constant and it should not increase after repeated etching.
3. If the crystal is deformed, e.g., by an indentation or a scratch, there should appear an increased density of pits around the deformation site and preferably the pits should delineate the slip rosettes.

The inhomogeneities in the grown crystals are revealed by etching because of reactions at inherently different rates at the inhomogeneity sites. The structural defects like point defects, line defects, inclusions, segregated area, 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 optical techniques.

The successful application of etching depends upon several factors. Among them, some important factors are as follows:

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 regent.
4. The length of time the specimen is etched.

As far as the etching reagent is concerned it should possess the following characteristics:

1. The reagent should be of such composition that it will give good all round results and reveal the greatest number and variety of structural characteristics, 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. Thus, the selective etching should enable one to study only specific defects.

2. The reagent should be simple in composition and stable so that its concentration will not change appreciably upon standing or during use at room temperature and also if possible, at moderately higher temperatures.

3. The reagent should have constant characteristics at a particular temperature so that the conditions of etching can be easily reproduced. The temperature and time of etching are also important factors to be decided in the etching process.

(a) Temperature of etching : The rate at which the etching reagent attacks the specimen, depends upon 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 reproducible results to carry out etching experiments only at definite temperatures.

(b) Time of etching : The time of etching is perhaps one of the most important factors contributing to successful etching and attendant appearance of the structure enabling their derailed study possible with the help of optical techniques. For examples, for short time of etching as compared to that appropriate for a particular material, the etch 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 upon the conditions of the specimen (i.e. normalized, hardened, etc.) and the temperature of the reagent.

4. The reagent while acting on the specimen should not form products which will 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 or facets 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 (001) of $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ (where x = 0.2, 0.3, 0.4), it was found after several trials that the etchants developed by the present author possessed most of the properties discussed above and was well suited for revealing dislocations.

It is well known that for metals the necessary ingredients of an etchant are generally an oxidant and a complexant which may, respectively, react with the specimen surface and dissolve the products formed. Nitric acid is a well known oxidant for etching of metals and in the present case also, it was found to be a well suited oxidizing agent for etching of the cleavage plane (001) of $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ (where x = 0.2, 0.3, 0.4) single crystals. It was also observed that the crystal surface is question has a high tendency to corrode and frequently to capture the reaction products, as also evident from the earlier reported results on etching of the pure InBi crystals. This fact poses a severe difficulty in developing a successful etchant. However after several trials two new dislocation etchants have been developed which give reproducible results as discussed below. 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 (001) surfaces.

ETCHANT A FOR $InBi_{1-X}Sb_X$ (where x = 0.2, 0.3, 0.4) :

For the cleavage plane of $InBi_{1-x}Sb_x$ (where x = 0.2, 0.3, 0.4) after numerous trials a dislocation etchant was developed which gives reproducible results. Some of the systematic stages of trials are stated in Table – 1. The best results are obtained with the etchant consisting of 1 part of solution A + 20 part of glacial acetic acid. Here solution A consists of 1 part saturated solution of citric acid +1 part of concentrated HNO_3 (70%) +10 part water (distilled). The minimum etching time to produce well-defined point bottomed square pits at room temperature was about 40 second.

Although the etch pattern produced by the etchant bears a general character of dislocation etch – pits, namely, the point bottomed geometry, it is essential to establish its reliability as a dislocation etchant. There are a few standard tests, which were carried out.

One of the most important test applicable for the cleavage surface is to establish one to one correspondence between the etch pits

Table – 1

Effect of etchant composition one etching characteristics

No	Etchant	Etching Time in second	Etching Characteristics
1	1 part of saturated solution of citric acid + 1 part of con. HNO3 (70%)	20 Sec	Over – etched, surface corrosion
2	1 part of saturated solution of citric acid + 1 part of con. HNO3 (70%) + 10 part of dist. Water.	20 Sec	Over etching, but surface is less corroded
3	1 part of saturated solution of citric acid + 1 part of con. HNO3 (70%) + 10 part of dist. Water. + 6 part of glacial acetic acid.	30 Sec	Surface corrosion is decreased, irregularly shaped corroded pits
4	1 part of solution A + 5 part of glacial acetic acid where 'A' is 1 part of saturated solution of citric acid + 1 part of conc. HNO3 (70%) + 10 part of dist water	40 Sec	No corrosion, pits size is very small and tend to assume shape
5	1 part of solution A + 10 part of glacial acetic acid	40 Sec	Free of corrosion, Reaction slowed down, pits tending to shape (Fig. 1)
6	1 part of solution A + 20 part of glacial acetic acid	40 Sec	Well controlled slow reaction, point bottomed nearly square pits (Fig. 2)

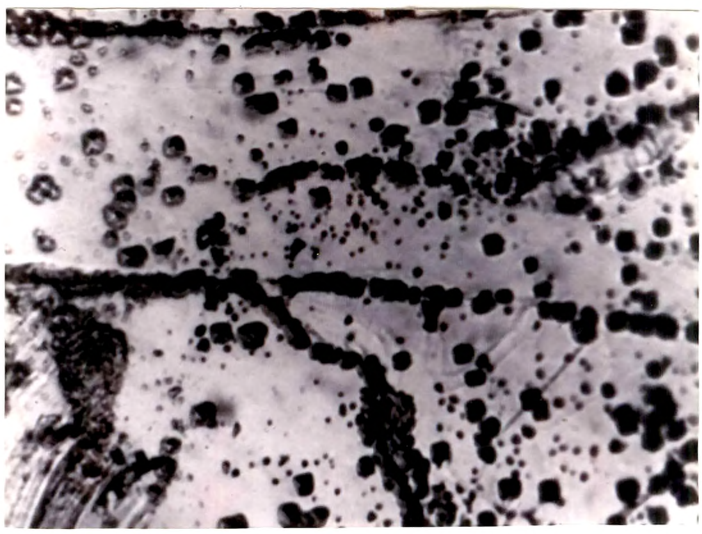

Fig. 1 **X 300**

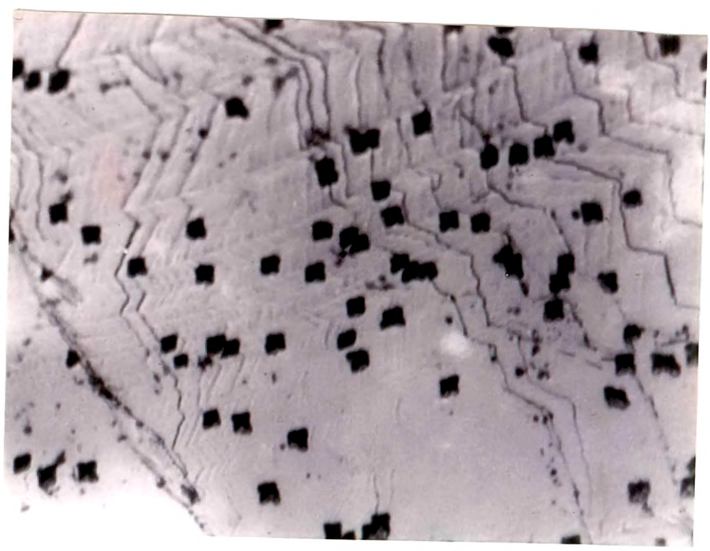

Fig. 2 X 300

produced on the cleavage counter faces.

Fig. 3(a) and Fig. 3(b) shows etch patterns obtained on oppositely matched cleavage faces. A fairly good one to one correspondence of etch pits on the two counterparts can be seen. From the figure it can be seen that both the position and the number of etch pits are in exact one to one correspondence.

Fig. – 4 shows a typical configuration of etch pit distribution. There are seen distinct rows of closely spaced etch pits as well as branching of rows. These rows resemble the low angle boundaries commonly observed in metallic and intermetallic crystals(16 – 22). Three rows of dislocations meeting at a point are known as triaxial boundaries. A model based on minimum free energy(23) for dislocation tilt boundary gives the relation.

$$n_a = n_b + n_c$$

where n_a, n_b and n_c are average density of pits along A, B and C branches respectively. This relation is satisfied with A, B and C designations indicated on the photograph in the figure above.

To test capability of the etchant to reveal fresh dislocations, the specimen was pin indented and etched. The resulting etch pattern near the pin indentation mark consists of increased number of pits along rows as shown in Fig. 5.

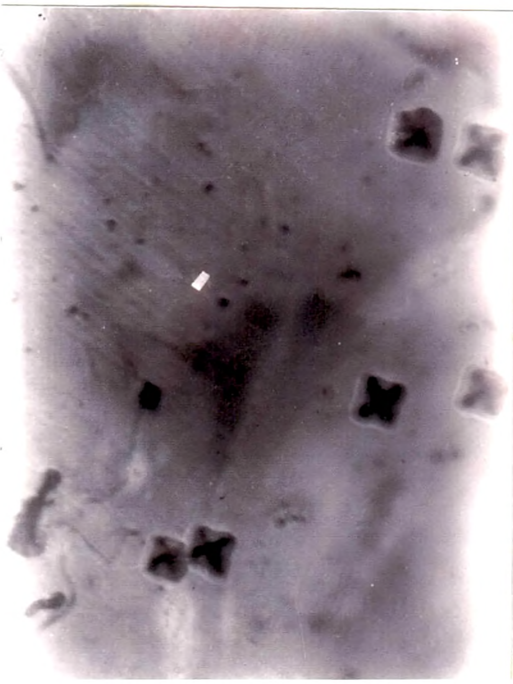

Fig. 3(a) X 500

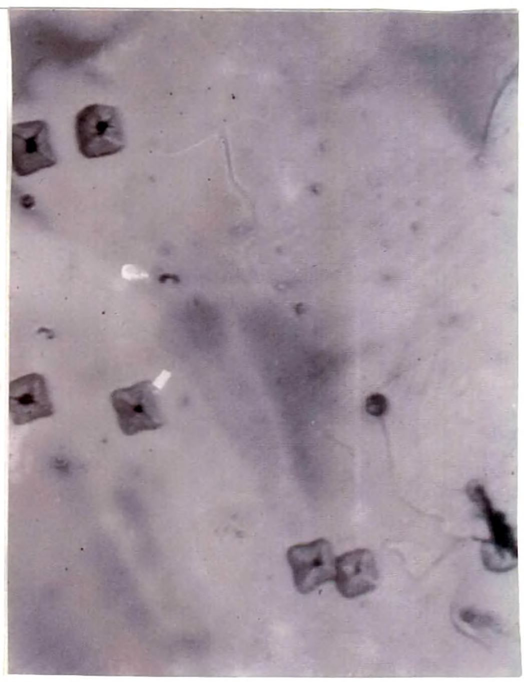

Fig. 3(b) X 500

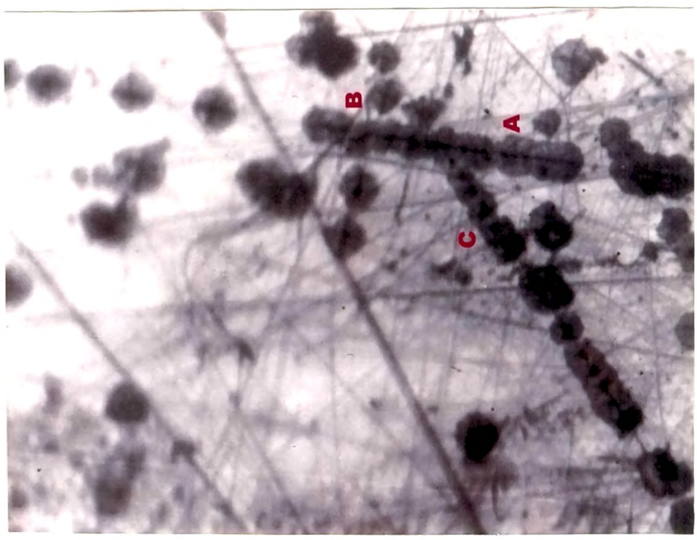

Fig. 4 **X 400**

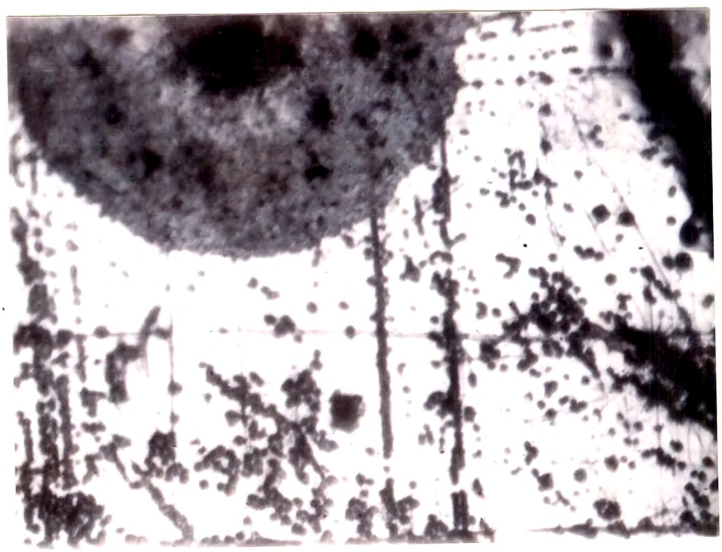

Fig. 5 X 200

Further tests for dislocation etchant, like scratching the surface and successive etching have been carried out successfully. Thus the chemical etchant of composition mentioned above can be reliably used to reveal dislocations intersecting the (001) cleavage plane of the crystals.

ETCHANT – B : For etching of $InBi_{1-x}Sb_x$ (where x = 0.2, 0.3, 0.4) another etchant was also developed by several numerous trials. The best composition obtained was as below.

1 part of solution A + 18 part glacial acetic acid where the solution A consists of 1 part saturated aqueous solution of Tartaric acid + 1.1 part of concentrated HNO_3 (70%) + 10 part of dist. Water. The minimum etching time to produce well defined point bottomed pits at room temperature was about 25 second. Some scattered etch pits produced by this etchant are shown on Fig. 6.

For testing the etchant as a dislocation etchant the tests like matching of etched cleavage faces, successive etching, delineation of low angle boundary etc., were conducted.

Fig. 7(a) and Fig. 7(b) show the etch patterns on oppositely matched cleavage faces. It can be seen that there is a good general matching of the pits. However, few mismatches are also observed which is due to reasons like uneven stresses developed at the time of cleaving the specimen, branching and bending of dislocations at cleavage,[24 – 25] etc.

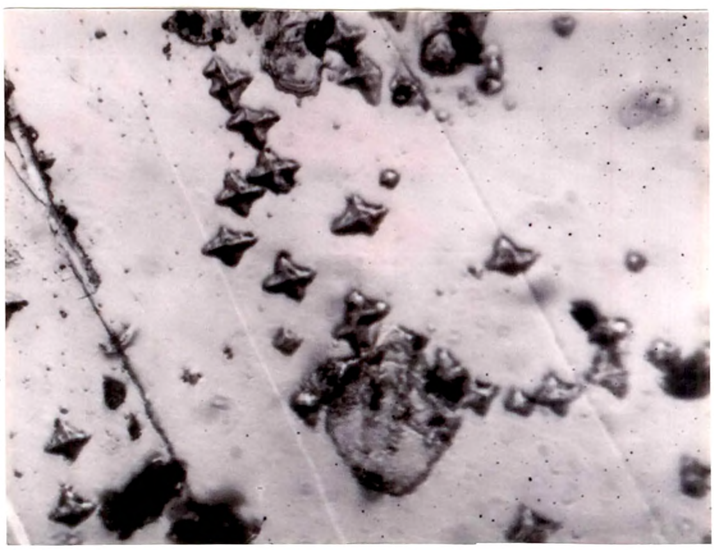

Fig. 6 X 400

Fig. 7(a) X 300

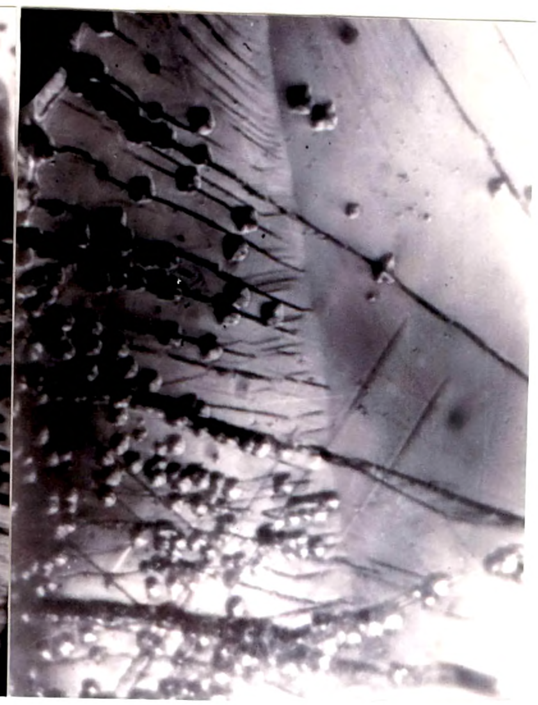

Fig. 7(b) X 300

The test of successive etching is based on the fact that a dislocation line cannot terminate within the crystal. Fig. 8(a) and 8(b) show the etch pit patterns obtained on the same region in the same cleavage surface etched for 25 second and 70 second, respectively, using this etchant. From the photograph 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.

Fig. 9 shows an example of triaxial boundary revealed by the etchant. As in the previous case relation $n_a = n_b + n_c$ is satisfied.

Fig. 10 illustrates a very good example of low angle boundaries delineated by etch pit rows.

Thus, it may be conclusively said that the etchant which is stated above is capable of revealing grown in and freshly produced dislocation intersecting the cleavage plane.

Although both the etchants A and B satisfactorily give reproducible results, etchant A is preferable to etchant B. This is because the reaction with etchant A is better controlled then the etchant B. Also the shape of etch pits obtained with etchant A is defined better than with etchant B as can be seen by comparing fig. 4 and 6. Hence for dislocation density measurements on $InBi_{1-x}Sb_x$ etchant A was used.

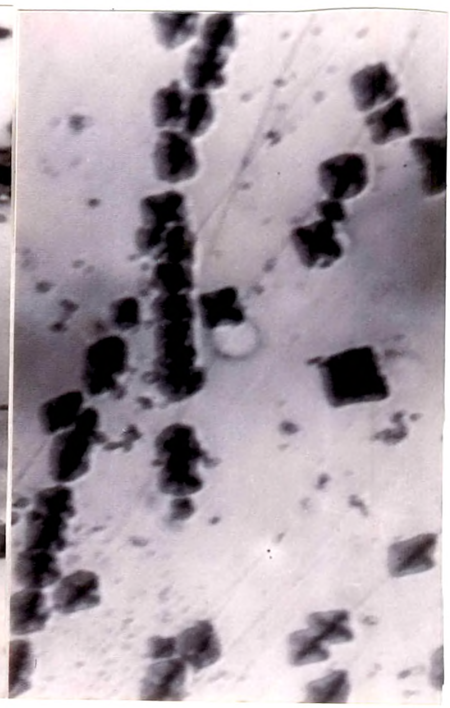

Fig. 8(a) X 450 Fig. 8(b) X 450

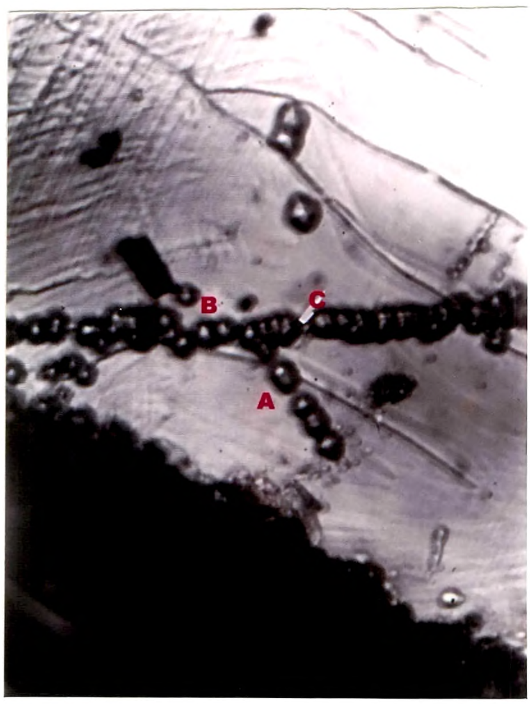

Fig. 9(a) X 400

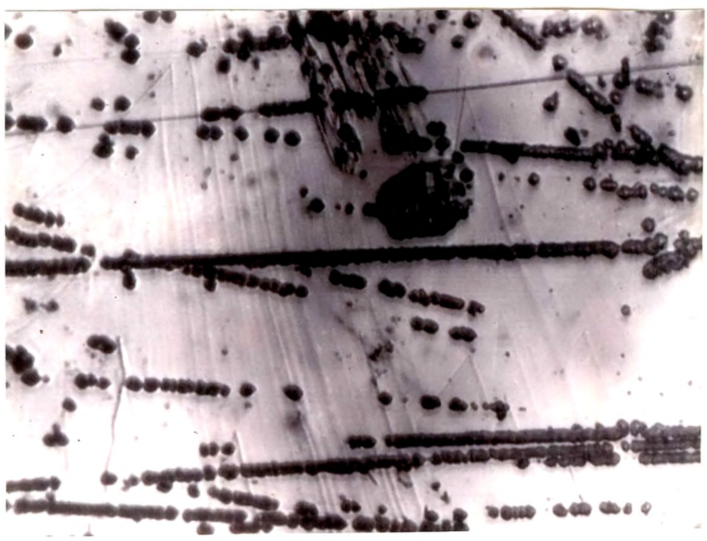

Fig. 10 X 200

ETCHANT A FOR $InBi_{1-x}$ Se_x (where x = 0.2, 0.3, 0.4) :

For the initial trials, concentrated HNO_3 (70%) was tried in various dilutions in water. Even at the lowest dilution there was general corrosion of the surface observed. To suppress this, acetic acid (glacial) was tried in different proportions with concentrated HNO_3 (70%). This composition of the etchant led to a systematic sequence of trials for the development of the dislocation etchant for these crystals. Some of the significant trials together with their etching characteristics are out lined in Table-2. It can be seen that among these trials the final satisfactory result obtained was by 1 part of solution A + 10 part of glacial acetic acid. Where the solution A consists of 1 part of concentrated $HN0_3$ (70%) + 5 part of distilled water. The minimum etching time was 10 second at room temperature. The etch pits were well- defined point bottomed and square in shape.

Thus the composition : 1 part solution A + 10 parts glacial acetic acid was found most suitable. For testing this etchant as a dislocation etchant, the tests like matching of etched cleavage faces, successive etching etc., were conducted. Fig. 13 (a) and 13 (b) show the etch patterns on oppositely matched cleavage faces. It can be seen that there is good over all matching of the etch pits. However mismatches are also observed. This may be due to reasons like uneven stresses developed at the time of cleaving the specimen, branching and bending of dislocations at the

Table-2

Effect of etchant composition on etching characteristics

No	Etchant	Etching Time in second	Etching Characteristics
1	1 part of concentrated HNO_3 (70%) + 5 part of dist. Water	25 Sec	Surface corrosion, pits are not shaped, Over etched.
2	1 part of concentrated HNO_3 (70%) + 5 part of dist. Water + 5 part of glacial acetic acid.	15 Sec	Approximate circular pits, corrosion.
3	1 part of solu. A + 5 part of glacial acetic acid. Where solu. A consists of 1 part Conc. HNO_3 (70%) + 5 part of dist. Water	10 Sec	Varying pits size, no surface corrosion (Fig. 11)
4	1 part of solu. A + 7 part of glacial acetic acid	10 Sec	No surface corrosion, square shape, point paltomed pits, nearly of the same size.
5	1 part of solu. A + 10 part of glacial acetic acid.	10 Sec	Size of pits increased, square point bottomed pits, no corrosion (Fig. 12).

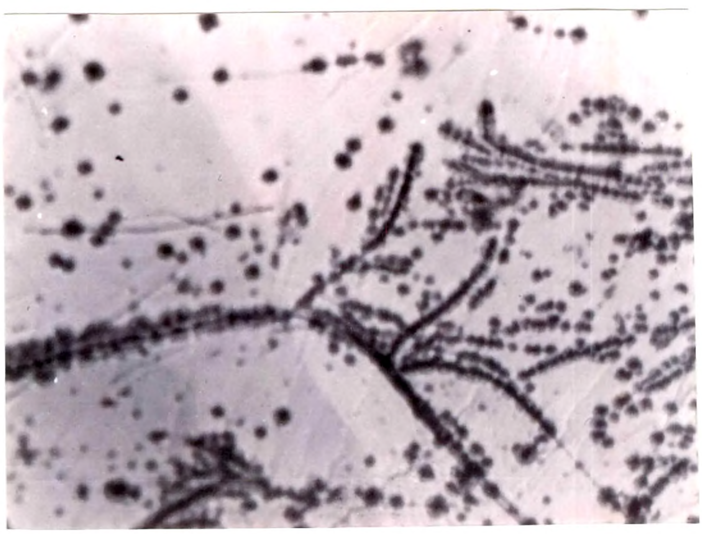

Fig. 11 X 300

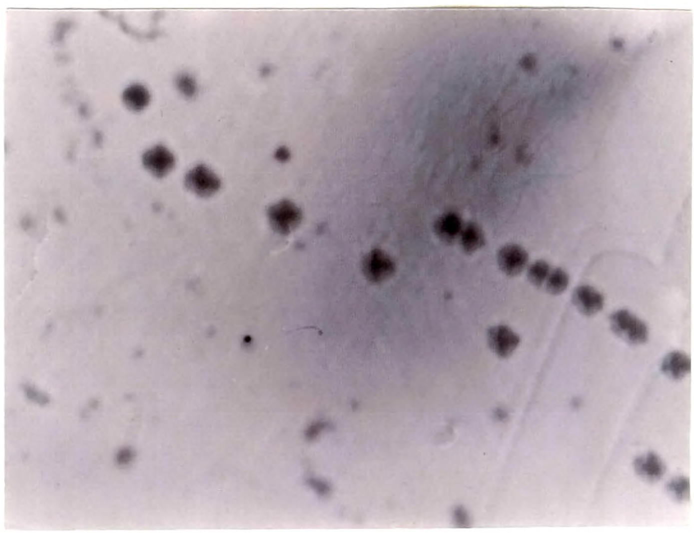

Fig. 12 X 400

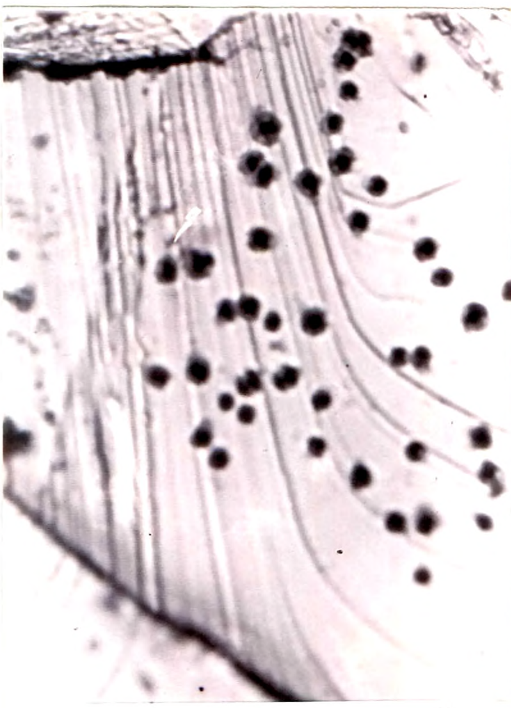

Fig. 13(a) X 400

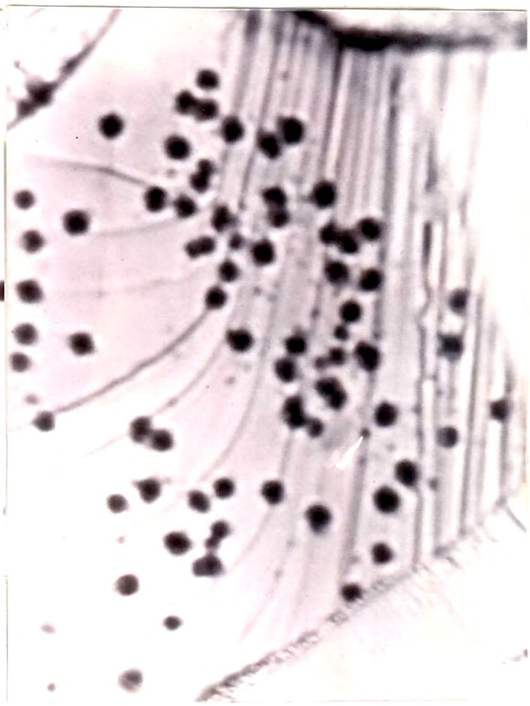

Fig. 13(b) X 400

cleavage plane etc..

Fig. 14 (a) and 14 (b) show the etch patterns obtained after successive etching for 10 second and 25 second, respectively. While the number of pits is the same in Fig. 14 (a) and 14 (b), the pit size in Fig. 14 (b) is larger indicating continuation of the dislocation lines into the depth of the specimen.

Fig.15 shows the etch pattern obtained around a scratch produced on the surface. The increased density and rearrangement of the etch-pits along the slip traces near the scratch show that the etchant is capable of revealing fresh dislocations also.

Fig. 16 shows a pin indented surface etched by the etchant. The resulting etch pattern near the indentation mark consists of well defined rows of etch pits as can be observed in the photograph.

Fig.17 is a typical etch pattern obtained by this etchant showing rows of etch pits which may be associated with low angle boundaries.

From the above results obtained with this etchant it can be concluded that the etchant is capable of revealing fresh and grown in dislocations intersecting the cleavage plane.

ETCHANT – B : For etching of $InBi_{1-x}Se_x$ where (x = 0.2,0.3, 0.4) second etchant was also developed by several numerous trials. The best composition obtained out of all composition was as below.

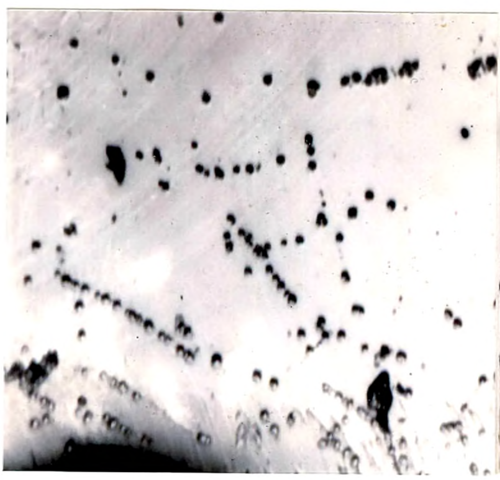

Fig. 14(a) X 350

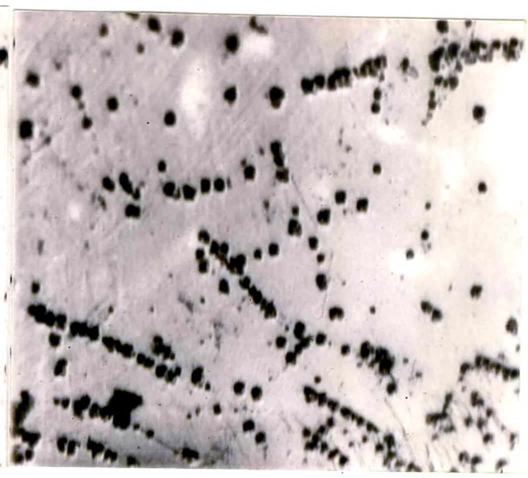

Fig. 14(b) X 350

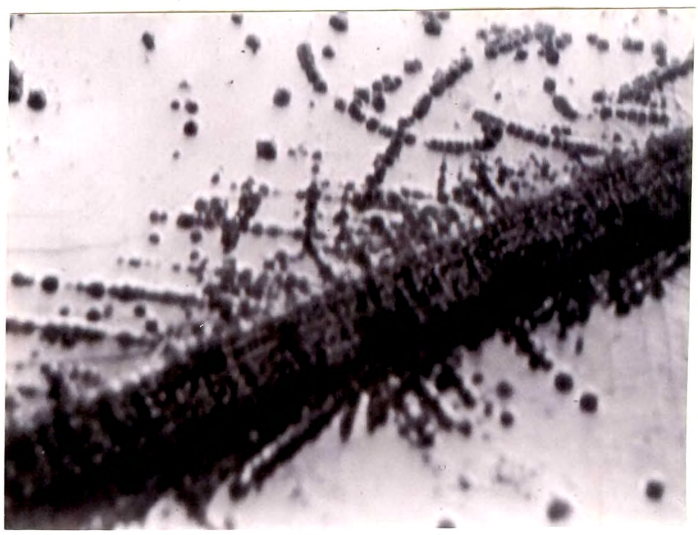

Fig. 15 **X 300**

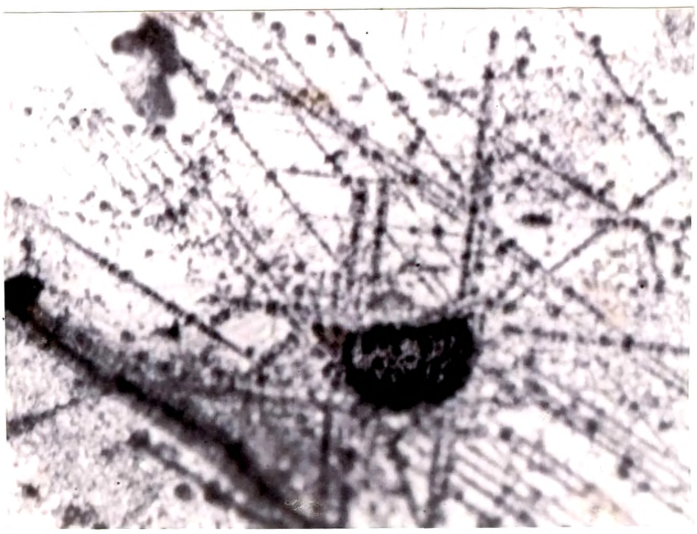

Fig. 16 **X 300**

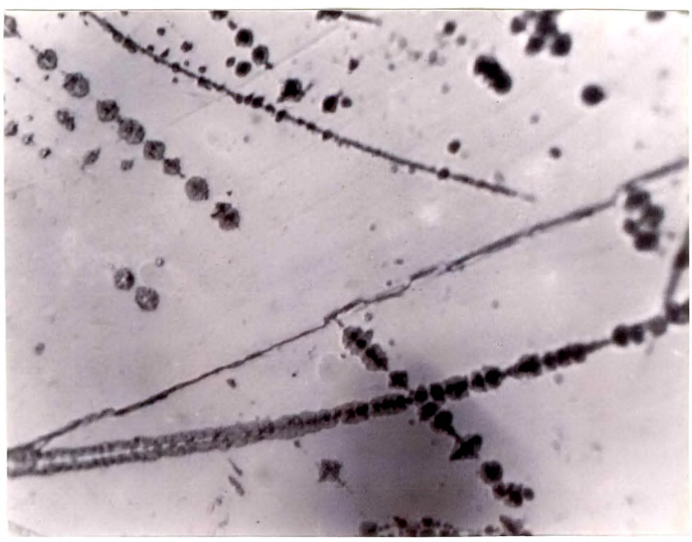

Fig. 17 X 350

1 part of solution A + 15 part of glacial acetic acid. Where the solution "A" consists of 1 part saturated solution of tartaric acid + 1.2 part of concentrated HNO_3 (70%) + 10 part of distilled water. The minimum etching time to produce well-defined point bottomed square etch pits at room temperature was about 15 second.

The test of matching of etched cleavage faces was conducted. Fig. 18 (a) and 18 (b) show the etch patterns on oppositely matched cleavage faces. It can be seen that there is a not a satisfactory matching of the pits except in a limited region of the surface shown.

Fig. 19 (a) and 19 (b) show the etch pit patterns obtained on the same region on the same cleavage surface etched for 15 second and 30 second, respectively, using the stated etchant. From the photograph it can be seen clearly that the pit size has increased to some extent with the etching time whereas their number has remained same.

Fig. 20 shows the etch pattern obtained around a scratch produced on the surface. The increased density and rearrangement of the etch pits along the slip traces near the scratch show that the etchant is capable of reveling fresh dislocation also.

It can be seen from the results that etchant B for $InBi_{1-x}Se_x$ crystals is not as good as etchant A. This is particularly because the matching of etch pits on cleaved counter parts is usually obtained to be

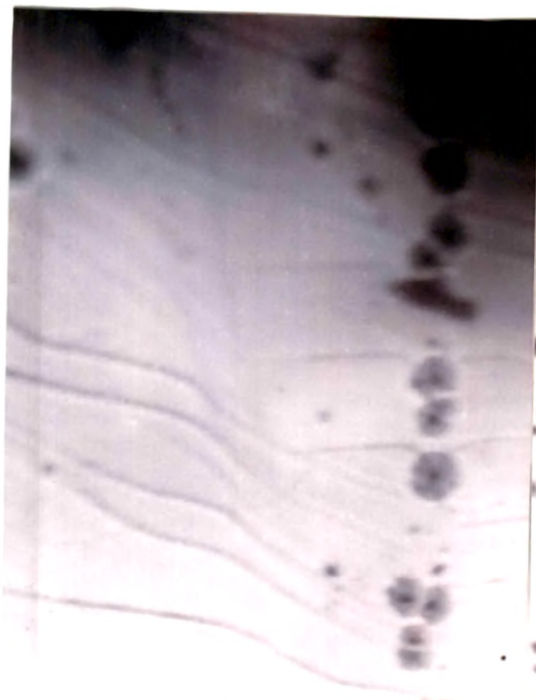

Fig. 18(a) X 450

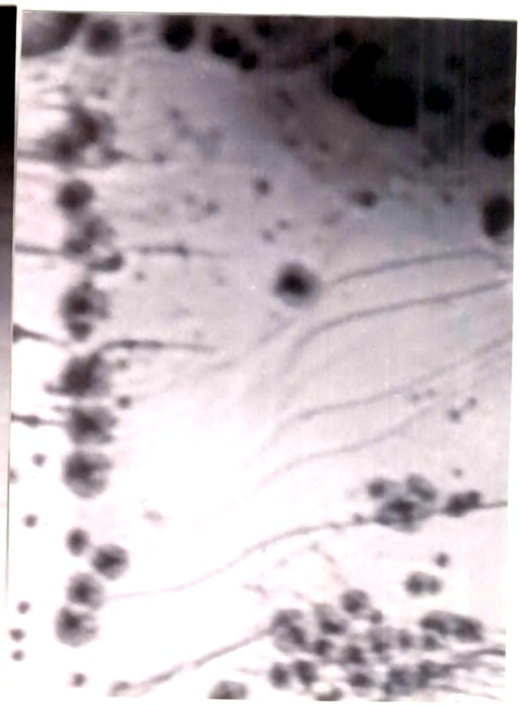

Fig. 18(b) X 450

Fig. 19(a) X 400

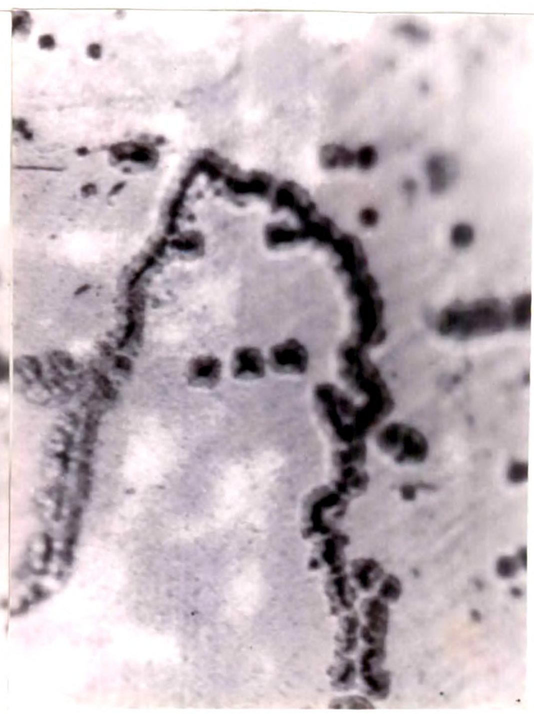

Fig. 19(b) X 400

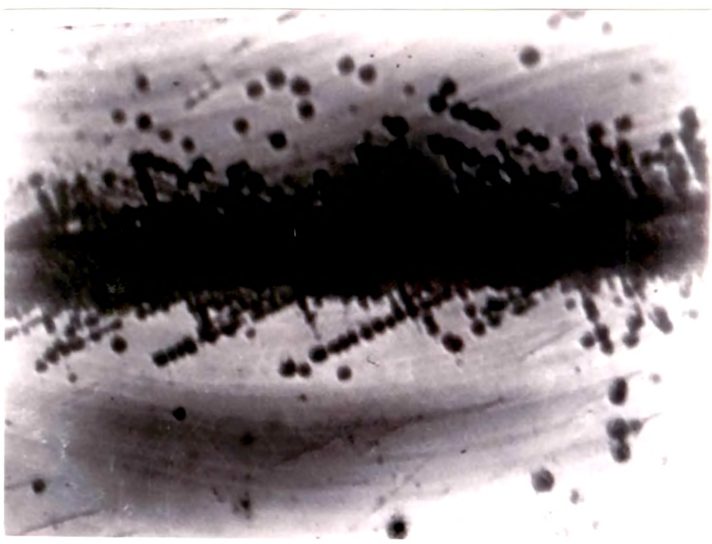

Fig. 20 X 300

poor implying the etchant to be undependable. Hence etchant A was used for dislocation density measurements on these crystals.

CONCLUSION :

The most reliable etchants developed by the author to reveal dislocations intersecting the cleavage planes of $InBi_{1-x}Sb_x$ (where x = 0.2, 0.3, 0.4) and $InBi_{1-x}Se_x$ (where x = 0.2, 0.3, 0.4) are, respectively,

(1). 1 part solution A + 20 part CH_3 COOH where solution A is 1 part saturated solution of citric acid + 1 part conc. HNO_3 (70%) + 10 part H_2O.

(2). 1 part solution A + 10 part CH_3 COOH where solution A is 1 part conc. HNO_3 (70%) + 5 part H_2O.

REFERENCE

1. Tayler, W.W. and Dash, W.C., J.Appl., 27 (1951) 1221
2. Dash, W.C., J. Appl. Phys., 27 (1956) 1193
3. Pfann, W.G. and Vogel, F.L., Acta. Met., 5 (1957)
4. Vogel, F.L. and Lovell, L.C., J.Appl.Phys., 27 (1956) 1413
5. Gillman, J.J., Trans. A. I. M. E., 206 (1956) 998
6. Gillman , J.J. and Johnston, W.G., J. Appl. Phys., 27 (1956) 1018
7. Amelinckx, S. and Strumane, G., J. Appl. Phys., 31 (1960) 1359
8. Hockey, B. J. and Mitchell, J.W., Phill. Mag., 26 (1972) 409
9. Faust, J.W., Sonderdruck aus der zeitschrift, Praktische Metallogrraphic, 3. J.q. Heft, 9 (1966) Seite 381
10. Sagar, A. and Faust, J.W., Sonderuck aus der zeitschrift, Praktische Metallogrraphic, 4. J.g. Heft, 1 (1967) Seite 35
11. Iwanaga, h., Shibata, N., Tanaka, A. and Masa, Y., J.Cryst. Growth (Netherlands), 84, 3 (1987) 345 – 8
12. Imashimizu, Y. and Watanabe, J.,J. Cryst. Growth (Netherlands), 99, 1-4 (1990) 2, 979 – 82
13. Roy, U. and Glassco, D., J.Cryst. Growth, 16 (1972) 227
14. Walter, H.U., J. Cryst. Growth, 19 (1973) 351
15. Bhatt, V.P. and Desai, C.F., Ind. J. Pure and Appl. Phy., 16 (1978) 960 – 962

16. Bhatt, V.P. and Pandya, G.R., J.Phys. "C" Solid StatePhysics. 6 (1973) 36

17. Sagar, A. and Faust, J.W., J.Appl. Phys., 38 (1967) 482 – 90

18. Sagar, A. and Faust, J.W., J.Appl. Phys., 23 (1966) 406

19. Amelinckx, S., Phil. Mag., 1 (1956) 269

20. Brown, D.M. and Heumann, F.K., J. Appl. Phys., 35 (1964) 1947 – 51

21. Yim Y.M. and Dismukes J.P., J.Phys. Chem. Solids Suppl., (1967) 187 – 96

22. Jain T.M., Pandya G.R. and Desai C.F., J. Cryst. Res. And Technol., 28 5 (1993) K 40 – K 43

23. Wernick J. H., Hobstetter J.N., Lovell L.C. and Worsi D., J. Appl. Phys., 29 (1958) 1101

24. Sagar, A. and Faust, J.W., J. Appl.Phys., 38 (1967) 482 – 90

25. Bhatt, V.P. and Pandya, G.R., J. Phys. "C", Solid State Physics. 6 (1973) 36