

# Crystal Growth and Dislocation Etching of $\text{Bi}_{0.75}\text{Sb}_{0.25}$ Alloy.

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**Abstract-**  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  single crystals have grown using the zone melting technique. The freezing interface temperature gradient of  $30^\circ\text{C}/\text{cm}$  has been found to yield good quality crystals obtained at the growth rate of  $0.5 \text{ cm/h}$ . The as-grown crystals have been observed to exhibit certain typical features on their top free surface. Using SEM, FTIR and EDAX technique have characterized the surfaces of the crystals and proportion. A new dislocation etchant has been developed to give reproducible etch-pitting on cleavage surface. Tests of this dislocation etchant have been carried out successfully to revealed the new dislocations and the dislocation density in the crystals of the order of  $10^{-4} \text{ cm}^{-2}$ . The results are discussed in detail.

**Index Terms**— Bi-Sb, Crystal growth, Etching, Triangular layer growth features, Optical band-gap, SEM, EDAX, FTIR

## 1 INTRODUCTION

Significant care has been taken in recent years to the BiSb single crystal alloys because they possess uncommon thermo magnetic effect at cryogenic temperature and semiconducting properties. At low Sb concentration Bismuth and antimony have rhombohedral structure often called the  $A_7$  structure of point group  $R\bar{3}m$ . They present two atoms per unit cell and similar lattice parameters, and the  $\text{Bi}_{1-x}\text{Sb}_x$  alloy has metallic nature and becomes more and more semimetal with antimony concentration exceeding about  $x = 0.1$ . The  $\text{Bi}_{1-x}\text{Sb}_x$  alloy system can be either a semiconductor or a semi-metal depending on Sb concentration [1-10]. Of at least equal importance to the chemical nature - the identity and quantity of the atoms present in a crystal - is the physical perfection - the position of the atoms in a crystal. Some authors were also grown Bi-Sb single crystals by the floating-zone technique [11].

In this paper we have grown  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  single crystals by zone melting method and the growth features were observed on the top free surface of crystals like triangular layer growth mechanism are also discussed. By using the FTIR, SEM, and EDAX techniques, we have discussed Energy gap, surface characteristics and proportion of alloy respectively.

## 2 EXPERIMENTAL DETAIL

Elemental materials Bi Sb, of 99.999 % purity were weighted to their stoichiometric proportion and sealed in a quartz ampoule under the vacuum  $10^{-5}$  torr. The ampoule containing charges were placed in a horizontal alloy-mixing unit at the temperature  $730^\circ\text{C}$  for 48 hours, during which it was continuously rocked and rotated for proper mixing and reaction. The ingot was then cooled to room temperature over a period of 24 hours.

Homogeneous single crystals of Bi-Sb alloy were grown by zone melting technique with a temperature gradient in the molten zone of about  $30^\circ\text{C}/\text{cm}$  and a growth velocity of  $0.5 \text{ cm/hr}$ . The degree of homogeneity was determined by etching studied and density measurement. On cleaving the crystal at  $0^\circ\text{C}$  by a sharp blade along the (111) plane it was found that the orientation of the crystal was almost parallel to the growth axis.

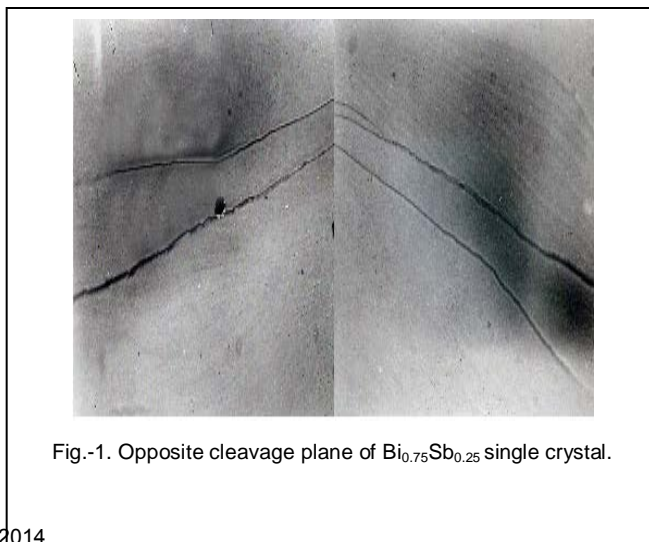


Fig.-1. Opposite cleavage plane of  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  single crystal.

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The features observed on the top free surface and on the cleavage plane were studied by optical microscope. Cleavage counter surface are shown in Fig.-1. It is apparent from cleavage lines that there is good one to one correspondence of surface patterns and more over lower the impurity concentration better is the perfection.

For IR measurement, solid sample was ground and mixed with hygroscopic KBr fine powder. This powder mixed sample was then placed in a mechanical dye to form a pellet, which can be placed in front of IR beam of the wave number range of  $510\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ , gives the absorption spectra. Using spectral analysis, the energy gap of the bulk material was measured and the surface morphology of crystals and constituent elements were identified by the SEM, EDAX detailed results are discussed.

### 3 Result and Discussion

Typical growth feature is shown in Fig.-2. Fig.-2 shows the transverse striations; there are two distinct sets of striations intersecting each other at an angle of  $120^\circ$ . Striations are due to motion of  $\{111\}$  family plane reported; these indicate that crystals probably grow by layer mechanism [12, 13]. The transverse striations were observed in almost all as-grown crystals. The crystals were subjected to successive etching and it was found that there was no change in the appearance of these striations. This indicates that they are not merely surface features but bulk phenomena.

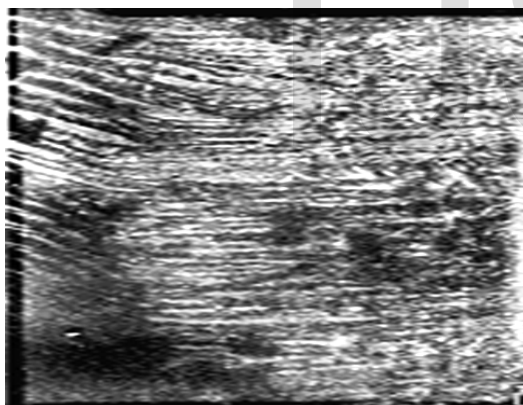


Fig.-2. The transverse striations; there are two distinct sets of striations intersecting each other at an angle of  $120^\circ$

The features indicate the surface orientation as to be consistent with symmetry. This parallel and equally spaced indicating crystallographic association. It is possible that some crystallographic plane like  $\{111\}$  may be responsible for these features. The observations indicate that the layer growth mechanism may be effective for the growth of  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  single crystal from the melt. The perfectness of the grown crystals in terms of dislocation content was estimated by the using dislocation etchant developed by the present authors after numerous trials. The characteristics of the etchant are described below.

The etchant consists of 4 part of concentrated  $\text{HNO}_3$  (70% AR grade) + 7 part of citric acid (saturated solution) + 1 part of distilled water. This mixture is capable of producing well-

defined triangular etchpits. The etching time was about 12 seconds.

There are the two very important characteristics of this etchant (i) Starting of the reaction is characterized by the evolution of the bubbles from the surface of the crystal, and (ii) the action of the etchant is slow enough for longer times of etching to be tried keeping the surface bright [14].

A dislocation etchant would reveal a low angle boundary on a crystal. In the present case a low angle boundary delineated by this etchant is shown in the Fig.-3. Some of the etchpits indicate dislocation in  $\langle 112 \rangle$  direction. Further a specimen was pin indented on the cleavage plane and subsequently etched. Rosettes of etchpits around the indentation mark were observed as an etching result indicating that the etchant can reveal freshly introduced dislocations as well. The average dislocation density of the crystals as measured by the etchpits count method was found to be  $3 \times 10^4\text{ cm}^{-2}$  on an average. [15]

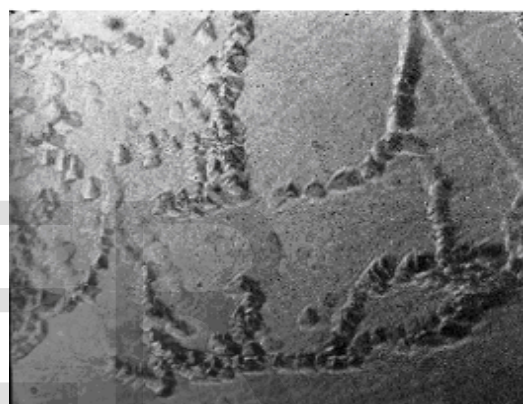


Fig.-3. A low angle boundary delineated by etchant.

Single crystals of  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  having dimension of 50 mm length and 7 mm diameter were obtained. EDAX as represented in Fig.-4 does the compositional analysis of  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  crystal, the EDAX analysis shows the presence of constituent elements.

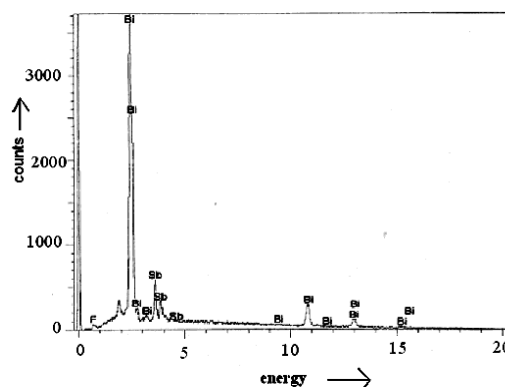


Fig.-4. Compositional analysis of  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  crystal, by EDAX

The plot of  $(\alpha hv)^2$  versus  $hv$  were used to evaluate the optical band gap, where  $\alpha$  = absorption coefficient and  $hv$  = photon energy. The plots are shown in Fig.-5 for  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  crystal. The plot is observed to be straight line in the region of high absorption side of the curves. The extrapolation of this linear part to the zero of abscissa has also been shown in the Figure-4, yielding the band gap value at the intercept on the  $hv$  axis  $0.078\text{eV}$  of the  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  crystal [16-18].

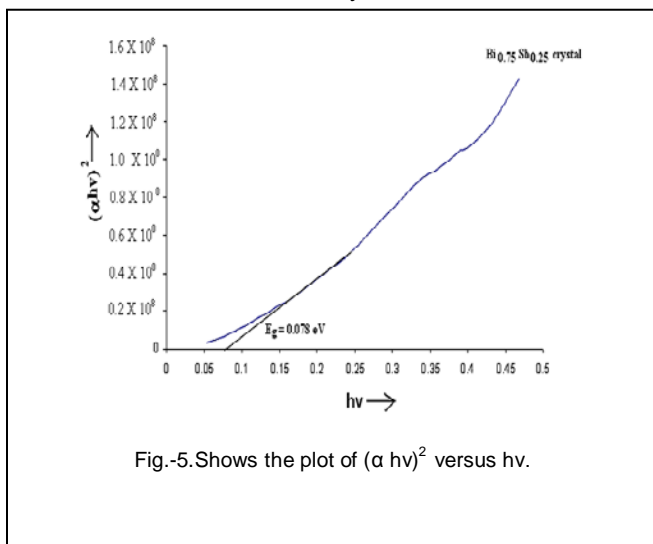


Fig.-5. Shows the plot of  $(\alpha hv)^2$  versus  $hv$ .

Freshly cleaved  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  crystals were used for SEM characterization. Fig.-6 indicate that the grown crystal are crystalline, shows that the number of cleavage line is very less so perfection of the crystal is more and also indicate the layer growth mechanism in  $\text{Bi}_{0.75}\text{Sb}_{0.25}$  single crystal is predominant.

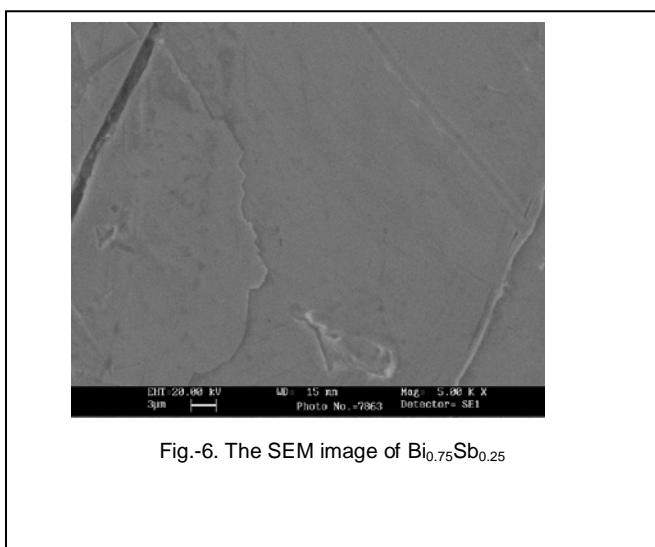


Fig.-6. The SEM image of  $\text{Bi}_{0.75}\text{Sb}_{0.25}$

## 4 CONCLUSION

Crystal growth mechanism is predominant by the layer growth mechanism. An etchant developed by the authors is capable of revealing the dislocations intersecting the cleavage plane. The crystal energy gap is of the order of  $78\text{meV}$ .

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