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Growth and Etching Studies on BiSF Single Crystals

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Bismuth sulpho fluoride was grown in sodium silicate gel solution using straight tube methods. Thiourea and bismuth trioxide dissolved in 10 N HF were used as the reactants. By etching the crystals, the dislocation morphology was studied.

INTRODUCTION

From a wide variety of current techniques for the growth of single crystals, the gel technique has gained considerable importance due to the simplicity and the effective growth of single crystals of compounds which cannot be easily grown by other methods. The work of Henisch[1] stimulated many workers to use the gel technique to grow crystals of variety of compounds which are sparingly soluble in water.

$A^{v}B^{vi}C^{vii}$ group compounds (where A^{v} is antimony or bismuth, B^{vi} is sulphur, senium or tellurium and C^{vii} is chlorine, bromine or iodine) are semiconducting ferroelectric materials. They exhibit certain other inherent characteristic properties such as electro-optic, photoelectric, piezoelectric, electrochemical and electromechanical[2]. These properties have been interlinked with each other ensuing other peculiar properties.

Among the V-VI-VII group compounds BiSF has been reported as useful material for device applications. This material has been used in light modulation time controlling devices and IR radiation converters[3]. Etching can be used as the versatile tool to probe the crystalline imperfections and also to have an idea in controlling the content of imperfections in crystals. The formation of etch pit depends mainly on the normal to lateral rates of dissolution of a given site[4]. The dislocation etch pits are formed when the etching reaction is sensitive to the energetics of the atoms at the crystal surfaces and also to the geometric configurations[5].

EXPERIMENTAL

A known quantity of thiourea solution of concentration ranging from 5 to 8% by weight was mixed with 100 mL of sodium silicate gel solution of density 1.04 g cm^{-3}. The gel solution impregnated with the inner reactant is acidified with 1N acetic acid and taken in straight tubes of different diameters (1 to 3 cm) and length (10 to 20 cm) and allowed to set. The period of gelation was varied from 1 to 24 h by changing the pH value of the gel solution. After gelation, solution of Bi_2O_3 (5 to 10 g) dissolved in 100 mL of 10 N HF is taken over the set gel. The outer reactant diffuses into the gel medium and reacts with the inner reactant giving rise to single crystals of BiSF.

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Arivouli *et al.*[6] have reported the etching studies of antimony sulpho iodide. They used both conc. and diluted HI acid and find the etch pit dislocation density. Etch pits were observed by them when con. HI was etched for 5 to 10 sec. A typical dislocation density of $10^5/cm^2$ was reported on most of the grown crystals.

In the present work, an effort was made to study dislocation densities of gel grown crystals by chemical etching method. Etching studies were done on the freshly cleaved (110) faces of BiSF. The crystals were etched with different etchants for different time of etching to reveal the pits at room temperature. The crystal surfaces were examined under an optical microscope.

RESULTS AND DISCUSSION

The growth of single crystals in gels at ambient temperatures was very effective for those materials having low solubility in water. The crystal growth in gel occurs as a sequence of controlled diffusion of ions through the inert gel medium, the reaction of the ions at some favourable rate to form crystal nuclei and finally growth of the nuclei into crystals of larger size. The crystal density is limited by diffusion of the reactants in the gel. In case of BiSF, when Bi_2O_3 dissolved in HF reacts with the inner reactant, thiourea, the entire gel mediun initially becomes greenish yellow[7]. After 20 days some glittering dots were observed in the gel medium. These dots started growing day by day and after 30 days single red crystals of BiSF upto 3 mm in size were obtained in straight tubes.

The distribution and arrangement of etch pits as shown by the arrays of etch pits and etch-pit clusters is typical of etch pits corresponding to the emergence points of dislocations. Moreover, inclusions due to some foreign material may also lead to etch pits. It was observed that the central regions of the faces of some crystals show a relatively high density of the nature of growth dislocations in gel grown crystals[8]. However, in order to draw some meaningful information from the etch patterns on doped crystals, the global dislocation density may be considered. In the case of BiSF, the etchants used, the observed etch patterns and the selective dislocation etch pits have been given in Table-1. The etch patterns on BiSF reveal that the crystals have been grown layer by layer in steps. The etch patterns obtained on the crystal surfaces as well as the surface features made on the as-grown crystals reval the growth of the crystal as in the form of layers.

TABLE-1
BiSF AND CHEMICAL ETCHING
Temperature : Room Temperature

Etchants	Etching parameters		Etch patterns
	Period	Concentration	
HF	30 sec	1 M	Fig (A)
HCl	3 min	6 N	Fig (B)
H_2SO_4	3 min and more	Concentrated	No effect
Acetic acid	3 min and more	Concentrated	No effect
Ethyl alcohol	30 sec	Concentrated	Fig. (C)
Ethanol	30 sec	Concentrated	Fig (D)

Selective etchant : Ethyl alcohol

Conclusion

Single crystals of BisF of size upto 5 mm have been grown in sodium silicate gel at room temperature. 10% Thiourea and 10 g of Bi_2O_3 in 100 mL of 10 N HF yield good crystals of large dimension. The gel grown BiSF crystal have been chemically etched and thereby the selective etchants have been investigated. The etch patterns have also been observed and studied. The formation of etch pits is found to depend upon the parameters of the etchants as well as the nature of the chemical etchants used.

ETCHING PHOTOGRAPHS

Fig. (A) Type of etch pits observed by etching (100) cleavage of BiSF using HF

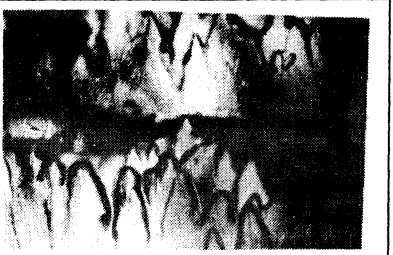

Fig. (B) Etch pattern observed when BiSF etched with HCl

Fig. (C) Etching BiSF with ethyl alcohol

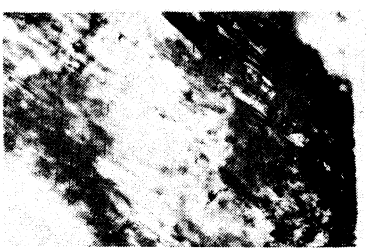

Fig. (D) Etch pattern observed when BiSF etched with ethanol

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