

Morphological Aspects of Bismuth Sulpho Iodide Grown by Silica Gel Technique

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Bismuth sulpho iodide (BiSI) has been prepared by the reaction of BiCl_3 dissolved in H_2SO_4 and acetic acid in silica gel. The morphology of some as-grown symmetrical crystals has been studied by optical microscopy. The growth morphology studies indicate that the grown crystals are needle-shaped, orthorhombic disphenoidal. The growth mechanism has been assessed.

INTRODUCTION

Crystals show a wide variety of morphology. Questions relating to variations and the relationship of different morphologies to the growth conditions of crystals have been a long and stimulating problem. The relationship between the morphologies of crystals and the growth conditions would help in understanding the kinetic processes of the growth mechanism. The morphology and morphology modifications of a variety of crystals have been studied earlier¹⁻³.

BiSI is one of the chalcogenides belonging to $\text{A}^{\text{V}}\text{B}^{\text{VI}}\text{C}^{\text{VIII}}$ compounds (where $\text{A} = \text{Sb, Bi, As}$; $\text{B} = \text{S, Se, Te}$ and $\text{C} = \text{I, Cl, Br, F}$). It is a semiconducting crystal which exhibits a number of interesting properties such as electrooptic, electro-mechanical, photoelectric, etc.⁴. This crystal has so far been grown from vapour, by slow cooling by Bridgman stock barger and by gel technique⁵⁻⁷. In the present paper the author reports the morphological variations in BiSI crystals and its relation to growth conditions.

EXPERIMENTAL

Single crystals of BiSI were grown by the gel technique. 10–15% of KI solution 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 was acidified with 1 N acetic acid and taken in straight tubes of different diameters (1–3 cm) and length (10–25 cm). The period of gelation was found to vary from 1 to 24 h. After gelation, solution of BiCl_3 (3–7 g) dissolved in 10 mL of H_2SO_4 of concentrations of 3–4 M was poured over the set gel. The outer reactant diffuses into the gel medium and reacts with inner reactant (KI) giving rise to black platelets of highly shining surfaces (Fig. 1).

Figure 2 shows the photograph of BiSI single crystal harvested in 30 days. Similar experiments were performed with thiourea and H_2S as the inner reactant and a mixture of Bi_2O_3 and BiI_3 as the outer reactants. Needles of BiSI crystals were obtained (Fig. 3) when H_2S was used as the inner electrolyte and BiI_3 in HI as the outer electrolyte⁸.

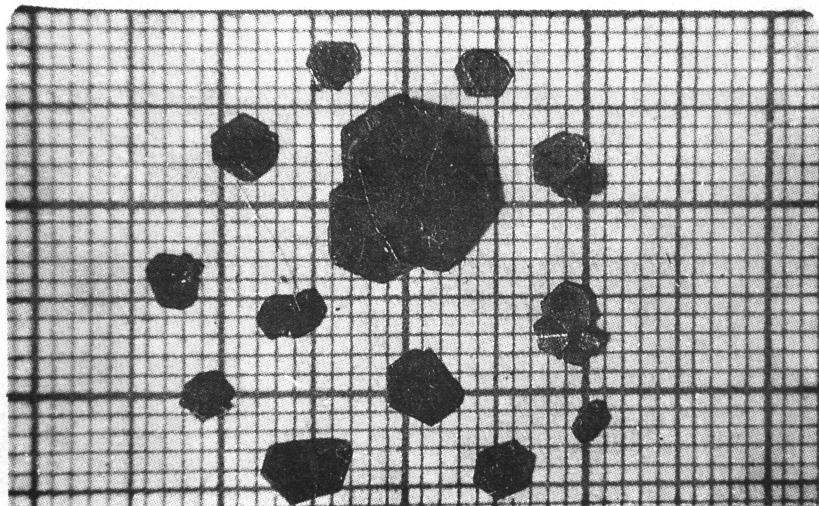


Fig. 1 Black platelets of BiSI

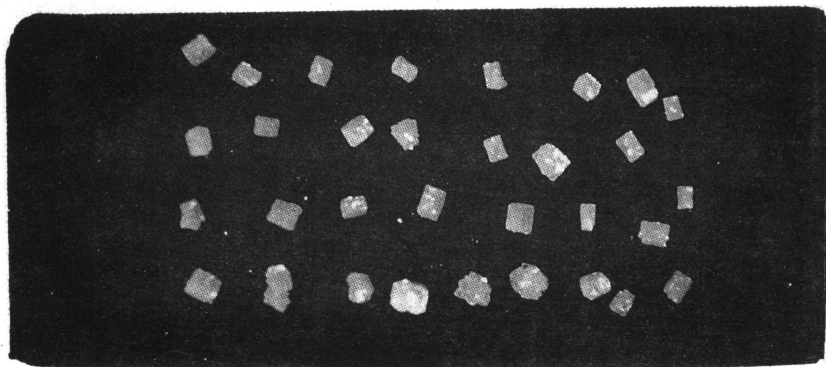


Fig. 2 BiSI crystals

RESULTS AND DISCUSSION

In the present investigations crystals with different morphologies were obtained at different depths in the growing test tubes and at different growth conditions. The morphology of the grown crystals is affected mainly by the concentration of the feed solution and pH of the system. Two types of morphologies of BiSI crystals were observed namely prismatic needle-shaped crystals and orthorhombic disphenoidal crystals (Fig. 4).

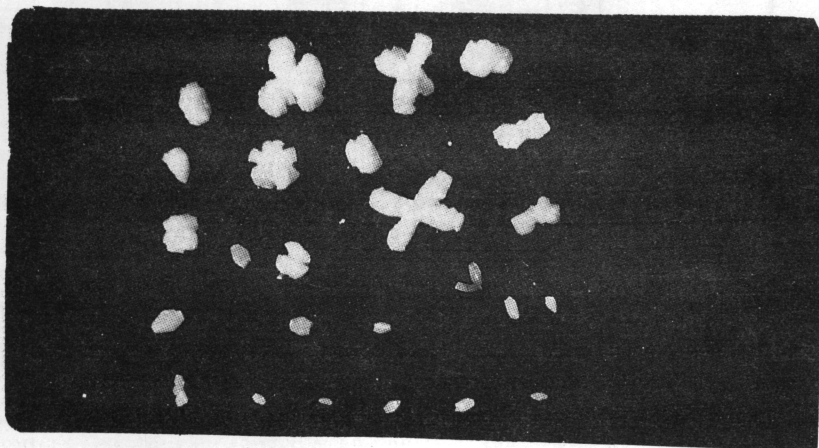


Fig. 3 Needleless crystals of BiSI



Fig. 4 Surface of orthorhombic disphenoidal crystals

Usually the nucleations of this type of crystals initiate in the region just below the gel-interface. They start growing from a bunch of nuclei with the diffusion of feed solution into the gel. With lapse of time, the thickness of the crystal increases with faster rate along (001) direction, which is the growth direction of BiSI crystals of different habits. This is due to the presence of diffusion field around the crystal tips

of the needle and the crystals grow into the supersaturated solution whereas the sides of the crystals are in contact with a largely exhausted solution⁹.

Fairly high concentrations of 2.0 M to 3.5 M BiCl₃ feed solutions and a fairly large amount of pH between 3 and 4.5 gave rise to rod-like orthorhombic disphenoidal type of crystals.

Influence of gel pH

In the absence of neutral gel, spontaneous nucleation occurring at the interface was very large. This spontaneous nucleation, in turn, affects the size of the growing crystal and thereby only 3 mm size platelets of BiSI single crystals were obtained. A solution of BiCl₃ dissolved in H₂SO₄ was poured over the set gel as the outer reactant. The effect of gel pH was studied and the results are as follows: pH range between 4.5 and 7.0 gave rise to prismatic needle-shaped crystals, while rod-like orthorhombic disphenoidal crystals obtained between 2.0 and 4.5 pH.

Effect of reactants

Crystallisation takes place for all concentrations of the reactants. In case of BiSI, good platelets of sizes upto 7–9 mm were obtained when 10% of KI was used as inner reactant and 5 g of BiCl₃ in 4 M H₂SO₄ as the outer reactant.

Habit modification depends on the phenomenon occurring on crystal surfaces. Diffusion of molecules on the surfaces of the growing crystal was an important parameter in this regard. The relative rates of surface diffusion on basal and prism faces are responsible for determining the habit in the very early stages of growth. The parameters such as concentration of feed solution, pH of gel, impurities on the solvent, temperature, etc., have considerable importance on the diffusion rate which ultimately influences the crystal morphology. In a steady state of concentration gradients, diffusion rate also becomes steady which favours the growth of well developed crystals.

Conclusion

Prismatic needle-shaped crystals, platelets and orthorhombic sphenoidal crystals of BiSI were obtained under different growth conditions. Increasing concentration of feed solution increases the linear growth along (001) direction. On introduction of neutral gel, platelets of BiSI of size nearly 7–9 mm were obtained in a period of 30–40 days when 10% KI was used as inner reactant and 5 g of BiCl₃ in 4 M H₂SO₄ as the outer reactant. The grown crystals were confirmed by X-ray analysis.

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