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Growth of bismuth sulpho-iodide single crystals from vapour

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Bismuth sulpho-iodide single crystals were grown from the vapour phase for various temperature gradients. When the temperature gradient was kept at 2° C cm^{-1} in a horizontal furnace a large polycrystalline boule was obtained. The boule consisted of thick platelets at the top and needles at the bottom. When the temperature gradient was decreased to 1° C cm^{-1} very good needles of length 2 cm and thickness varying from 0.5 to 2 mm were obtained. They grew as hollow needles in a vertical furnace. The grown crystals were of length 1.5 cm and thickness ranging from 0.5 to 1 mm.

1. Introduction

The V–VI–VII group compounds are ferroelectric semiconductors. Most of the members of these compounds are found to be orthorhombic with the space group D_{2h}^{16}. Bismuth sulpho-iodide (BiSI) is ferroelectric, electro-optic, electromechanical and photoelectric and has been grown from vapour [1–3], by slow cooling [4], by Bridgman–Stockbarger [5], by modified flux technique [6] and by hydrothermal method [7]. Due to the inherent property of the structure, they mainly grow as needles. Hollow crystals of BiSI have not been so far reported. Hollow crystals find importance for the fabrication of certain devices using electrodes attached to the inner and outer surfaces with favourable geometrical arrangement. The conditions under which BiSI grows as solid crystals and as hollow crystals have been investigated.

2. Experimental details

For the synthesis of BiSI, high purity elements (> 99.99%) of bismuth, sulphur and analar grade resublime iodine were used. They were mixed in the stoichiometric ratio and sealed off at a pressure of 10^{-5} torr in a glass tube of length 20 cm and diameter 1.5 cm. The temperature was kept at 20° C above the melting point of the compound for 4 h. It was cooled, powdered, annealed and powder diffractogram using Cu$K\alpha$ radiation was carried out. The reflexes were found to be in agreement with the literature values [1–3]. In the second run, the tube was kept at a temperature of 540° C for two days, then cooled to room temperature. The powder diffractogram revealed that bismuth sulpho-iodide had been formed.

About 15 g of the charge obtained in the first run was taken in a glass tube of length 20 cm and diameter 1.2 cm and sealed at 10^{-5} torr. The ampoule was kept in a two zone horizontal furnace and the growth zone was cleaned by initially keeping the temperature higher than the source zone. In the growth experiments, the temperature difference between the two zones was varied from 10 to 40° C keeping the source zone at constant temperature (520° C) and varying the growth zone temperature. In the second series of experiments, about 20 g of the material obtained in the second run was taken in an ampoule length of 20 cm and diameter 1.5 cm, sealed off at 10^{-5} torr and kept in a two zone vertical furnace.

3. Results

In the first series of experiments, employing horizontal furnace, the observed morphologies of the crystals are summarized in Table I. For the temperature difference of 40° C polycrystalline boule consisting of large size platelets of dimensions 5 mm × 0.5 mm was obtained. The top surface of the boule consisted of platelets of different dimensions and the bottom of the boule consisted of bundles of needles orienting along the crystal axis (c-axis). Fig. 1 shows the polycrystalline boule and the platelet is shown in Fig. 2. When the temperature difference between the two zones was increased beyond 40° C condensation of thin films of bismuth triiodide occurred. It is due to the fact that BiSI melts incongruently and dissociates into BiI_3 and

TABLE I Effect of temperature gradient on the morphology of the single crystals of BiSI

Ampoule dimensions (cm)	Temperature difference between source zone and growth zone (° C)	Morphology and dimensions
length 20 diameter 1.2	10	needles, length 1 to 1.4 cm, thickness 0.5 to 1 mm.
	20	needles, length 2 cm thickness 2 mm.
	30	needles, length 1.4 cm, thickness 1.1 mm.
	40	polycrystalline boule with platelets, and needles.
length 20 diameter 1.0	30	needles length 0.8 to 1 cm, thickness 0.5 to 1 mm.

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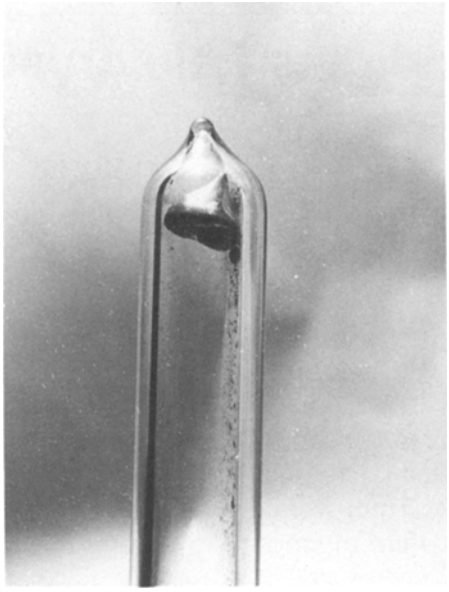

Figure 1 Polycrystalline boule of BiSI.

Bi_2S_3. Scanning electron microscopy (SEM) analysis was done using a Cambridge Steroscan 250. Fig. 3 shows an elevated strip observed on the surface of the needle. The distribution of bismuth, sulphur and iodine was uniform confirming the formation of a single phase. Chemical analysis was also carried out to confirm the respective elements in the compound. In order to study the etch pit dislocation density, the crystal was etched with a mixture of dilute hydrochloric acid and concentrated nitric acid in the ratio 10 : 1. Elongated triangular etch pits were observed at the dislocation sites (Fig. 4). Higher amounts of nitric acid decompose the material. The grown crystals were examined by the Laue back reflection technique and showed that they were single crystals with orthorhombic point group symmetry. X-ray single crystals analysis showed that crystals have lattice parameters of $a = 0.872$, $b = 1.053$ and $c = 0.418$ nm.

In the second set of experiments employing the vertical furnace, the growth zone was kept at 480° C and the source temperature was kept at 530° C. After 16 h hollow crystals of length 1.5 cm and thickness ranging from 0.5 to 1 mm were obtained. For lower temperature differences there was practically no crystallization in the growth zone. The grown crystals are

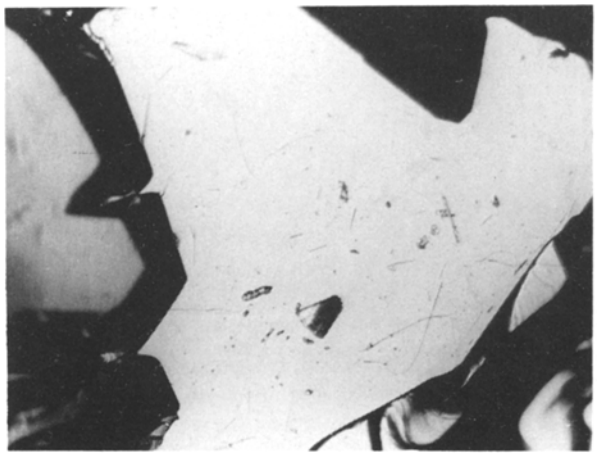

Figure 2 Platelets of BiSI (× 10).

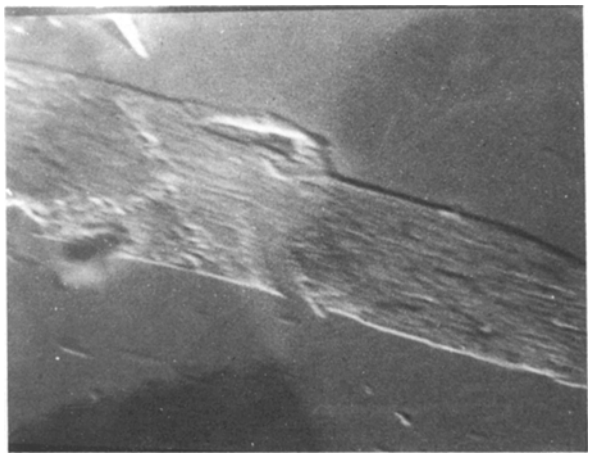

Figure 3 An elevated strip observed on the surface of the BiSI needle (× 1400).

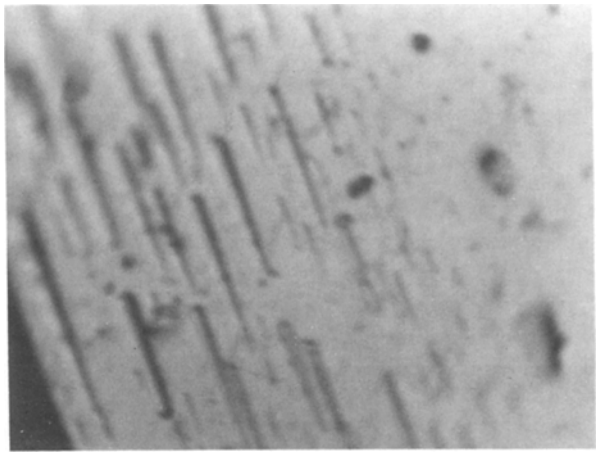

Figure 4 Etch pits on the surface of BiSI (× 300).

shown in the Fig. 5. The hole exists all along the lateral surface of the needle. Fig. 6a and b show BiSI whiskers grown on the BiSI needle. Fig. 7 shows a needle with a bend at the centre of the needle. Fig. 8 shows the surface of the crystal by cleaving the needle. Fig. 9 shows the hollow needle with a jagged end.

No generally accepted model exists for the explanation of the kinetics and mechanisms of hollow crystals with closed or open lateral surface. Some workers [8–10] reported that impurities are responsible for their growth while others explained [11, 12] in the absence of impurities. Park and Reynolds [13] pointed out that the hollow crystals are produced when new

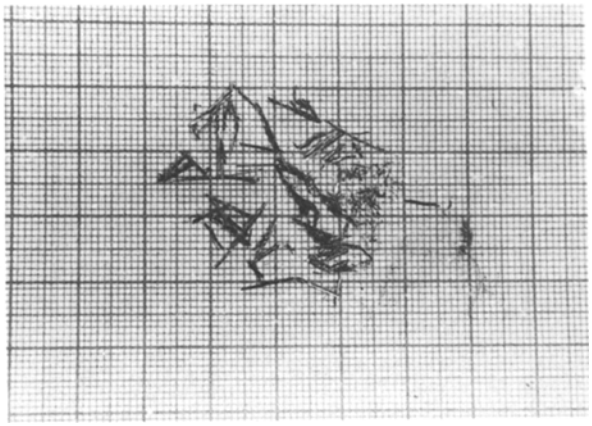

Figure 5 Hollow needles of BiSI (× 1).

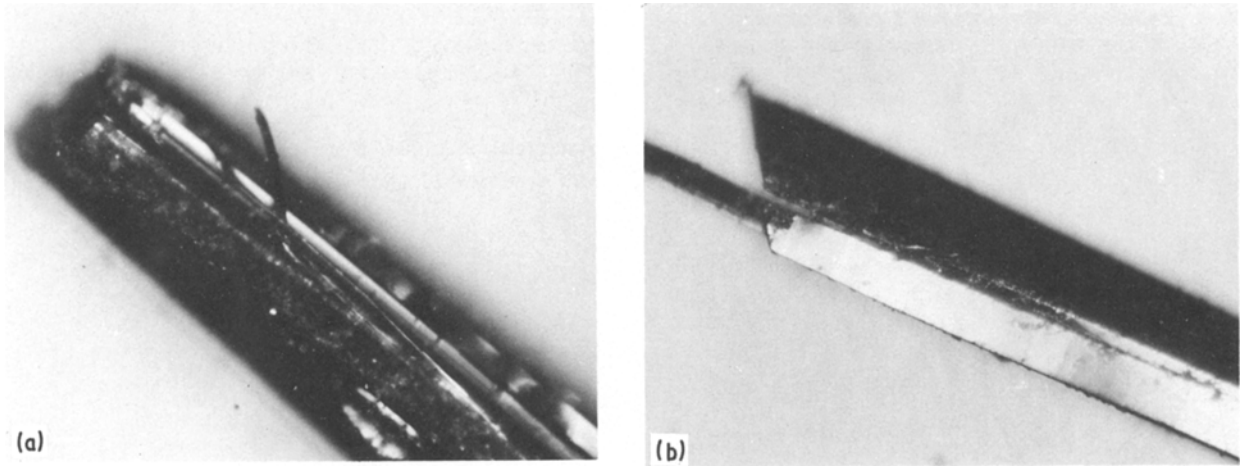

Figure 6 (a) and (b) BiSI whiskers grown on the hollow needle (× 125).

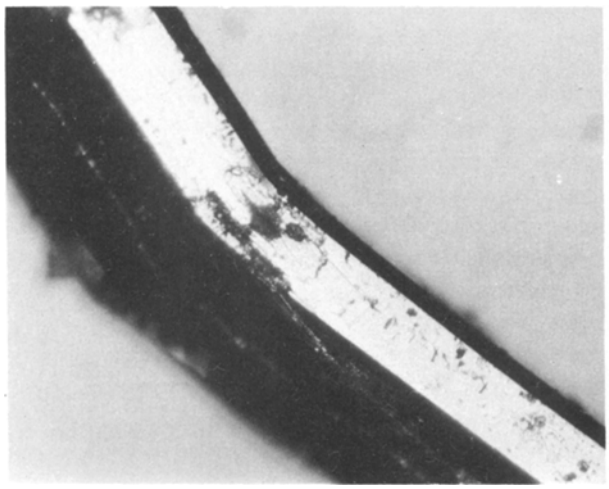

Figure 7 Needle with a bend at the centre (× 125).

Figure 9 Needle showing the jagged end (× 125).

layers generated near the edge of the crystal deplete the supply of the material before the layer can reach the centre of the growing surface. Sharma [14] suggested the origin of whisker growth to a cluster of screw dislocations of same sign. Gaumann and Bohac [11] explained the hollow nature on the basis of thermal and photoelectric properties. In Figs 6a and b the whisker growth is due to a difference in supersaturation at that place and the growth of these whiskers depends on supersaturation. When the supersaturation is high, the length is shorter. This is due to the growth being suppressed by the two-dimensional nucleation frequently occurring on the lateral surfaces of whiskers. Similar result was obtained by Hayashi and Saito [15] in the vapour growth of magnesia whiskers. The growth begins by two-dimensional nucleation from one of the vertices in two directions (on two neighbouring edges) and branches out. When these two branches overlap due to heat difference of crystallization, the supersaturation at that place is reduced and so the bending occurs at the centre of the planes (Fig. 7). The surface of the cleaved hollow BiSI (Fig. 8) shows the bundles of whiskers orienting along the needle axis (*c*-axis). It is found that the hollow crystals grow at very high supersaturations.

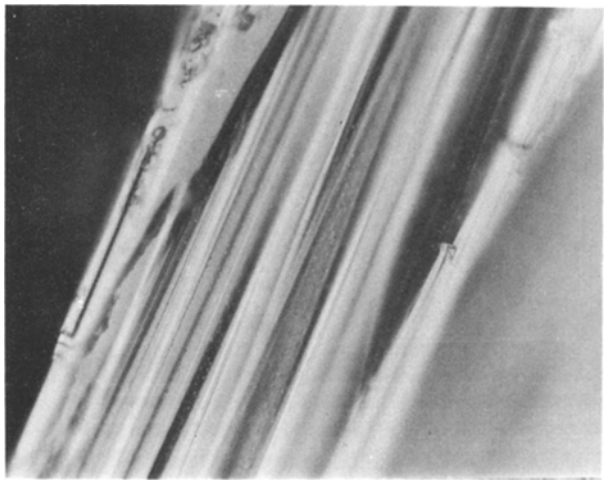

Figure 8 Surface of the cleaved needle (× 1350).

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