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Growth of antimony sulpho iodide single crystals from vapour

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Antimony sulpho iodide single crystals have been grown from vapour as solid crystals and also as hollow crystals. The morphology is found to depend on the temperature gradients. The optimum conditions for the growth of hollow crystals are determined.

1. Introduction

The ferroelectric semiconducting SbSI has interesting properties such as photoconductivity and electro-optics with a large anisotropic behaviour along the *c*-axis [1–4]. In the ferroelectric phase it belongs to the point group mm2 and goes through a phase transition at 293 K to the paraelectric phase with an orthorhombic point group mmm. A wide variety of growth techniques have been reported [5–11] for the growth of single crystals of SbSI and in all the methods needle morphology predominated due to its inherent characteristics of the growth rate anisotropy. Recently, Raman *et al.* [12] have grown SbSI single crystals in sodium silicate gel at room temperature. The growth faces are oriented along the vertical zone ($h\,k\,0$) due to the presence of a double chain ($Sb_2S_2I_2$) extending along the *c*-axis. The present work describes some of the interesting features observed from the vapour-grown single crystals of SbSI prepared from the elements antimony, sulphur and iodine.

2. Experimental details

The initial compound was prepared by fusion of the constituents, weighed in the stoichiometric ratio without any excess of iodine or sulphur. The powder diffractogram values of this compound agreed with those reported in the literature [13, 14]. In the growth experiments, about 15 g of this sample was placed in a glass ampoule of length 20 cm and diameter 1.5 cm, sealed at a pressure of 10^{-5} torr and kept in a horizontal two-zone furnace. The growth zone was cleaned by initially maintaining the temperature higher than the source zone. The temperature difference between the two zones was varied from 10 to 30° C, keeping the source zone temperature at 410° C.

In the second series of experiments, about 20 g of the sample was placed in glass ampoules of length 20 cm and diameter 1.2 cm. The temperature in the source zone was kept at 410° C while the growth zone temperature was 340° C.

3. Results and discussion

In the first series of experiments, single crystals of length 1.5 cm and thickness up to 0.3 mm were obtained after 2 days. The typical growth patterns are as shown in Fig. 1, for the crystals grown with a temperature difference of 10 to 20° C. In Fig. 1 very thin needles are seen towards the end of the growth zone and thick needles preceding the source zone. This may be due to the higher supersaturation in the region towards the source zone. Needles of thickness 0.4 to 1.2 mm were obtained for a temperature difference of 30° C.

Fig. 2 shows brick-like elevations observed on the (0 0 1) face. Fig. 3 shows the sculptured shape patterns on the (1 1 0) face of the needle. This may have developed due to the stresses occurring during growth and supersaturation differences.

In the second series of experiments, hollow crystals, as shown in Fig. 4 were obtained after 4 to 5 h. The tips of some of the hollow crystals were tapered. Whiskers were found to grow in between the open lateral surface of the crystal with the growth layers on the bottom surface. Spiral-like layers were also observed on one of the hollow edges. The surface of the cleaved hollow SbSI is shown in Fig. 5. Since the (1 1 0) face consists of densely packed sheets of $(Sb_2S_2I_2)_n$, its growth is possible on account of Van der Waals reaction between sheets which may be considered as the basis for the formation of two-dimensional nuclei. The (0 0 1) face is a K-face [15] and therefore grows rapidly because of the ease and independence of the joining of the structural parts by the mechanism of normal growth. Owing to very high anisotropy in growth rates along [0 0 1] and [1 1 0], some of the materials are pushed out, thereby creating

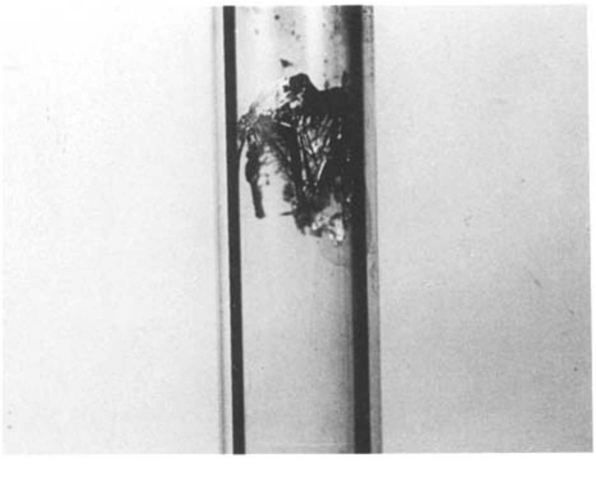

Figure 1 SbSI grown with a temperature difference of 10° C.

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Figure 2 Brick-like elevations observed on (0 0 1) face (temperature difference 10° C) × 823.

Figure 3 Sculptured patterns on the as-grown surface, × 925.

crevices which then become hollow as they propagate when the crystal grows.

4. Conclusions

Antimony sulpho iodide single crystals grow as solid as well as hollow crystals when grown from the vapour. The morphology of the crystals depends on the temperature gradients. The surface morphology of the crystals described by many authors [16, 17] did not have complete faceting and were often imperfect, containing inclusions and voids. However, the surface of the SbSI needles, as observed by the present authors, did not show any such imperfections. The growth of hollow crystals is explained on the basis of crevice creation.

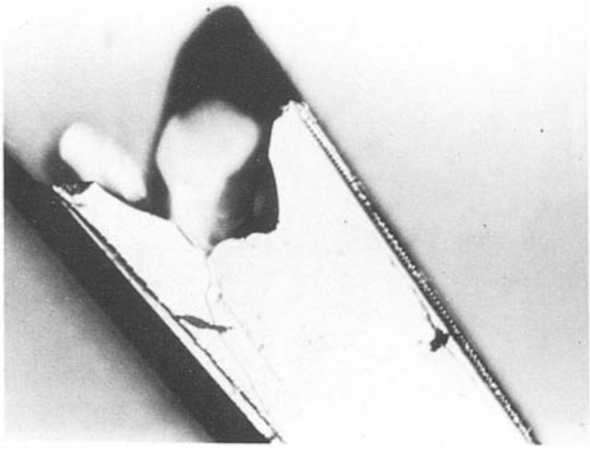

Figure 4 Hollow crystal of SbSI, × 125.

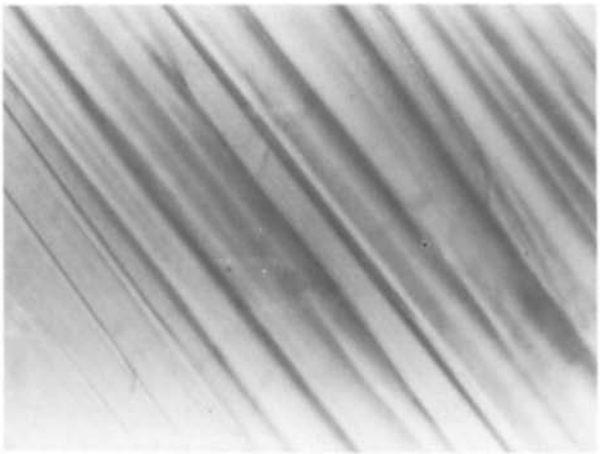

Figure 5 Cleaved surface of the hollow crystal, × 950.

The crystals grown were confirmed by X-ray diffraction analysis and found to be single crystals with an orthorhombic point group of symmetry with lattice parameters $a = 0.851\,\text{nm}$, $b = 1.012\,\text{nm}$ and $c = 0.411\,\text{nm}$. The presence of the respective elements was confirmed by spectral analysis.

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