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Growth of bismuth seleno iodide single crystals from the vapour

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Single crystals of bismuth seleno iodide (BiSeI) have been grown for the first time from the vapour by the temperature oscillation method, and the crystals obtained compared with those grown by the sublimation method. Single crystalline large-size boules and platelets were obtained by the temperature oscillation method, depending on the temperature gradients. Single crystallinity of the needles and platelets was confirmed by X-ray analysis, and the crystals were confirmed as BiSeI using an energy dispersive spectrum analyser.

1. Introduction

Bismuth seleno iodide (BiSeI) is one of the V–VI–VII group compounds showing bond anisotropy due to its chain structure. It belongs to the orthorhombic system with the space group Pbnm. The BiSeI structure consists of chains of $(Bi_2Se_2I_2)_n$ parallel to the *c*-axis [1], the bonding between neighbouring chains being weak anion–cation bonding; direct anion–anion bonding is made difficult because of the long distance between the anions in the adjacent chains. The exchange forces within the chains are much larger than the forces between the chains [2]. The phase diagram of BiSeI shows that this compound melts congruently at an intermediate point; it also shows a characteristic change from congruent to incongruent melting at higher Bi_2Se_3 composition, agreeing well with the partial dissociation reaction

$$3\ BiSeI \leftrightharpoons Bi_2Se_3 + BiI_3$$

at 500° C as observed by Turyanitsa *et al.* [3]. The ternary compound BiSeI is formed when the ratio of Bi_2Se_3 and BiI_3 is 1 : 1, and melts congruently at $540 \pm 3°$ C [3]. BiSeI has photoelectric [4], ferroelectric [5] and piezoelectric [2] properties, and shows both n- and p-type conductivity depending on the method of growth: crystals grown by chemical transport reactions show n-type [4] conductivity and crystals grown by the Stock-barger method show n- and p-type conductivity [3]. The value of the energy gap also depends on the growth conditions; 1.3 eV by the Stock-barger method and 1.32 eV when grown by the chemical transport method [4]. Aleshin *et al.* [6] have measured the rate of mass transport during crystallization of SbSeI, BiSI and BiSeI from the vapour in closed ampoules. They found that there is an increase in mass transport when iodine or chalcogen is used, compared to the pure sublimation method.

The supersaturation in the vapour growth (in which the source and growth temperatures remain constant during the whole growth process) remains unaltered and so unable to form small number of crystals through primary nucleation by reducing the supersaturation. Moreover, in the vapour growth involving a stationary temperature profile procedure, the constitutional undercooling is a drawback which appears as a result of both large supersaturations and the presence of mass convection in the vapour.

Al-Alamy abd Balchin [7] have grown layer-type crystals by iodine transport when the growth end of the ampoule is subjected to a periodic upward fluctuation of temperature during the growth period. Their best results were obtained when the amplitude of the temperature fluctuation was of the same order as the magnitude of the temperature differences between the source and crystal. Paorici *et al.* [8] also obtained best results by the time–varying temperature profile procedure for growing $CuInS_2$, $CuGaS_2$ and $AgIn_5S_8$ compounds.

BiSeI single needles were grown from the melt [2, 9, 10], from the vapour [5, 11] and by the hydrothermal method [12]. In all these methods needle morphology predominated. We know of no report in the literature on the growth of bulk crystals of BiSeI from the vapour.

2. Experimental techniques

BiSeI was synthesized using bismuth (99.999%), selenium (99.99%) and analar grade (99.9%) resublimed iodine by vacuum fusion. The compound was confirmed by taking a powder diffractogram using a Reich Seifert powder diffractometer employing CuK_α radiation with a nickel filter and a quartz monochromator. The reflections were found to agree well with the literature [1]. About 20 g of the sample were placed in a quartz ampoule of length 20 cm and diameter 12 mm with a pointed end and sealed off at a pressure of 10^{-5} torr. A two-zone horizontal furnace which can be controlled independently by two controllers was used for the present study. Experiments were carried out by the sublimation method with and without temperature oscillation for different degrees of supersaturation or temperature gradients, keeping the source zone temperature constant at 560° C in the case of the non-oscillatory method. The time–temperature profile for the temperature oscillation method is as shown in Fig. 1.

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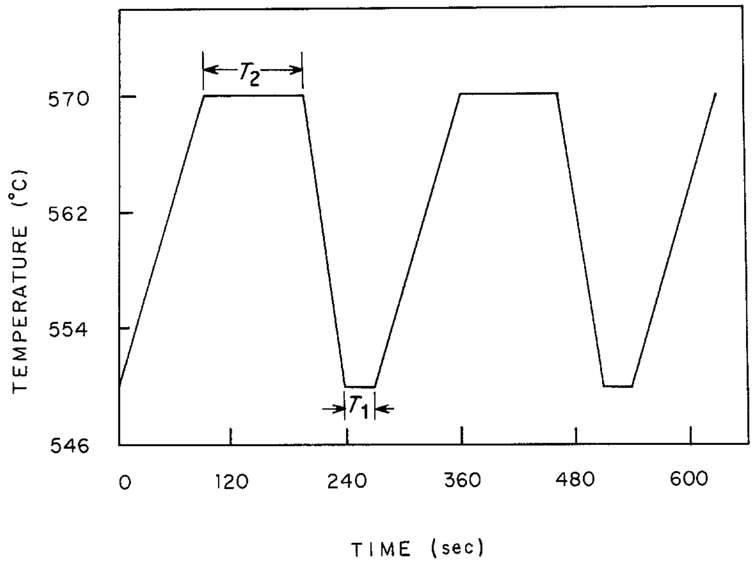

Figure 1 Time–temperature plot for the oscillation method.

3. Results and discussion

Thick needles, as shown in Fig. 2, were obtained for a temperature difference of 40° C from the non-oscillatory source zone growth technique. On changing the temperature difference to 50° C, needles emerging from the tip of the pointed end of the crucible were obtained as shown in Fig. 3. A temperature difference of 60° C between the two zones produced a polycrystalline boule. In some cases dendritic crystals [13] were also obtained. Upon further increasing the temperature difference, polycrystals with very small platelets with hollow needles on top, as shown in Fig. 4, were obtained. The platelets were found to show (1 1 0) faces, the growth of which can be realized either by the mechanism of formation of two-dimensional nuclei or on dislocations and other crystal surface defects which are confirmed by the following observations. The surface of the as-grown platelets were studied using Leitz optical microscope, and revealed growth spirals as shown by the optical micrograph (Fig. 5) on the (1 1 0) face [14]. Fig. 6 shows the macrosteps on the surface of the (1 1 0) face obtained for the temperature difference of 60° C. The higher magnification of Fig. 6 shows that each step is a collection of layers.

Some of the platelets showed dendritic features at the edges. In some of the platelets, growth spirals were obtained. It is observed that in the initial stage, growth of the platelets is dendritic [13] due to the presence of high supersaturation which favours dendritic growth. Supersaturation is decreased as growth proceeds and there exists quasi-equilibrium between the crystal and vapour. Now the regions between the dendritic arms are filled in and the growth of flat, smooth crystals finally proceed by the layer growth mechanism (Fig. 6) which helps growth of larger sized platelets [15].

Good results were obtained by the temperature oscillation method for two different temperatures in the growth zone. Crystals were grown for different T_1 and T_2 (Fig. 1) and for very large T_2, needle morphology predominated. Figs 7 and 8 show BiSeI crystals without needle morphology, from the two different growth zone temperatures. For a growth zone temperature of 510° C, 3 mm diameter (up to 5 mm) and 12 mm length crystals were obtained with a convex top surface showing that the crystal–vapour interface is convex thus providing a good nucleation site. For a growth zone temperature of 520° C platelets of dimensions 20 mm × 10 mm × 6 mm were obtained (Fig. 9).

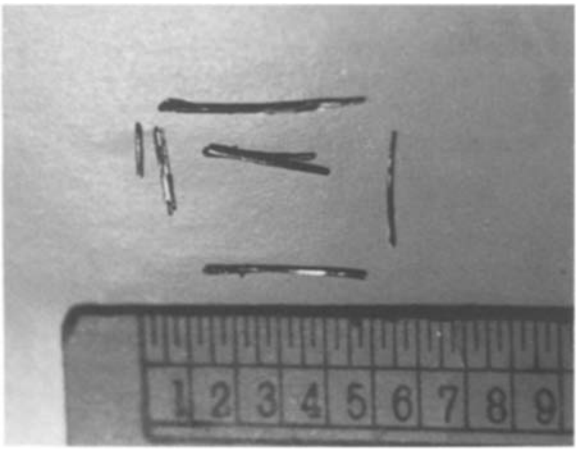

Figure 2 BiSeI needles.

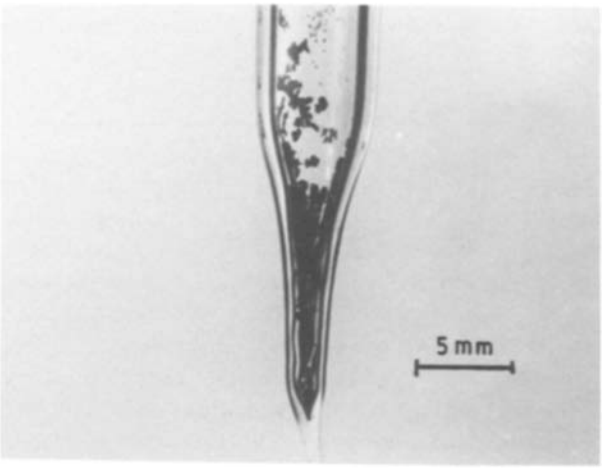

Figure 3 Needles emerging from the tip of the pointed end of the ampoule (temperature difference 50° C).

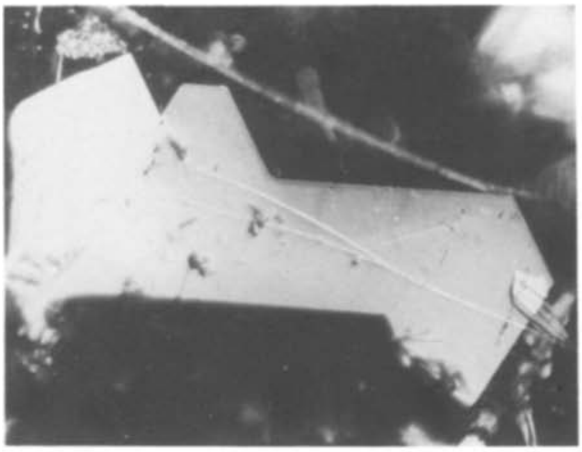

Figure 4 BiSeI platelets with hollow needles on the top, × 200.

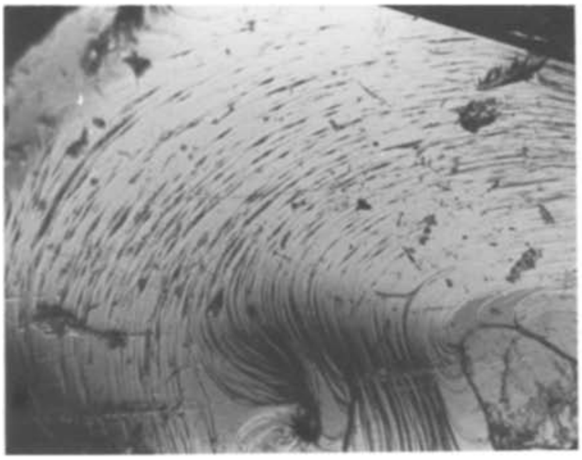

Figure 5 Step-like layers, × 800.

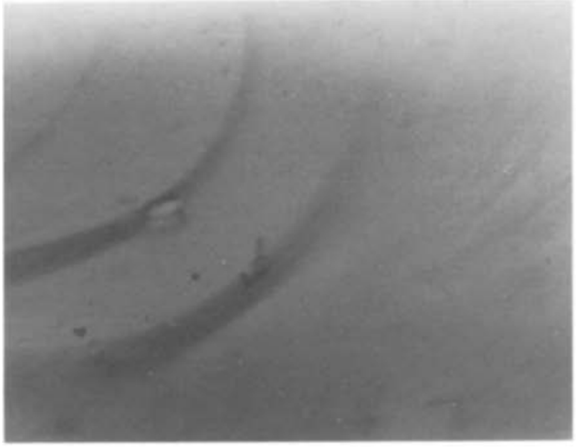

Figure 6 Macrosteps on the as-grown surface of the platelet, × 675.

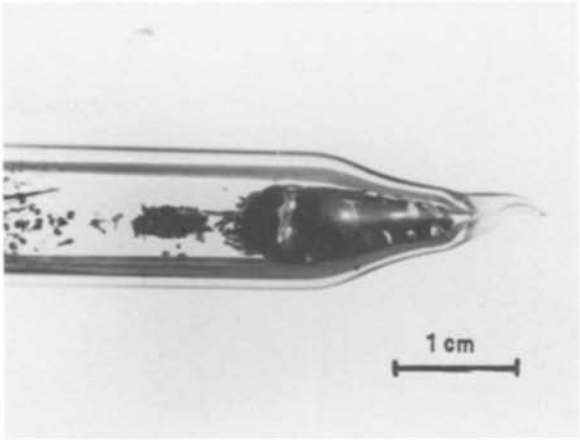

Figure 7 Platelets of BiSeI (growth zone temperature 520° C).

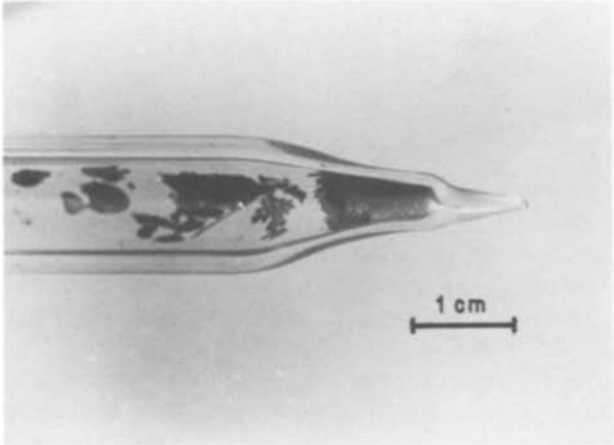

Figure 8 BiSeI boule (growth temperature 510° C).

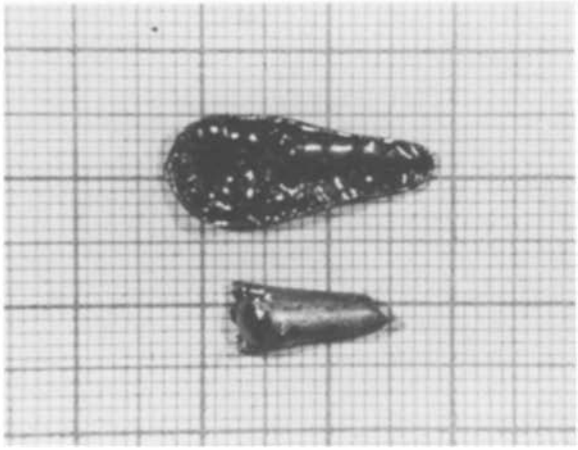

Figure 9 Larger crystals of BiSeI.

TABLE I

Method	Morphology	Crystal size	Reference
Slow cooling	Needle	Length up to 20 mm	[9]
Stock-barger	Needle	$20 \times 5 \times 5\,\mathrm{mm}^3$	[3]
Stock-barger	Needle	$10 \times 4 \times 2\,\mathrm{mm}^3$	[2]
Hydrothermal	Needle	length 25 to 40 mm thickness 0.3 to 0.7 mm	[12]
Chemical transport	Needle	$10 \times 1.2 \times 1\,\mathrm{mm}^3$	[4]
Sublimation	Needle	length 10 to 20 mm diameter 0.1 to 0.2 mm	[11]
Sublimation	Needle	$25 \times 2 \times 1\,\mathrm{mm}^3$	Present work
	Platelets	$5 \times 1 \times 0.5\,\mathrm{mm}^3$	Present work
Sublimation (Temperature oscillation method)	Platelets	length 12 mm diameter 3 mm (up to 6 mm) $20 \times 10 \times 6\,\mathrm{mm}^3$ (up to $25 \times 10 \times 8\,\mathrm{mm}^3$)	Present work

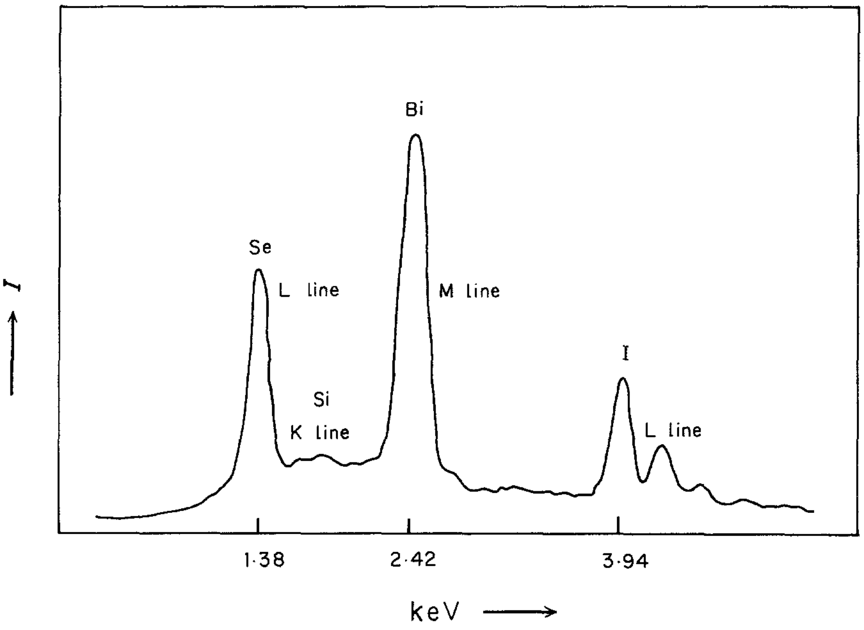

Figure 10 Spectral analysis of BiSeI crystals.

Triangular growth hillocks were obtained on etching the (1 1 0) face of the platelet with ethyl alcohol for 10 sec. The platelets grown by the temperature oscillation method were easily cleaved parallel to the (1 1 0) direction. The size and the nature of the crystals of BiSeI grown are summarized in Table I. The crystals were confirmed to be single crystals by the Laue technique and by viewing under a polarizing microscope. The respective elements in the single crystals of BiSeI were confirmed by spectral analysis (Fig. 10).

4. Conclusion

Both single crystal needles and platelets of BiSeI were grown from the vapour by the sublimation method. For very low supersaturations, needles were obtained, while on increasing the supersaturation polycrystalline boules with needles and platelets were obtained. The surface of the as-grown crystals revealed a layer growth mechanism. In the case of the temperature oscillation method, larger platelets, without needle morphology, were obtained. The size of the crystals was found to be improved by using the temperature oscillation method.

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