CHAPTER 3

GROWTH OF SbSI AND SbS$_{0.8}$$I_{0.2}$ CRYSTALS FROM MELT
BY TEMPERATURE FLUCTUATION TECHNIQUE
3.1 INTRODUCTION

Single crystals of SbSI have been grown by vapour phase techniques [1-6], hydrothermal methods [7,8], from aqueous solutions [9], by melt [10] and by flux [11-15] growth techniques. In all these methods, needle growth morphology has predominated with the length of the needles being parallel to the c-axis of the orthorhombic crystal. Since such a wide variety of growth techniques have produced the same growth morphology, it can be deduced that the growth rate anisotropy in this crystal is a characteristic property of the material, a conclusion which is also evident from its structure [11].

However, growth from the non-stoichiometric melt containing 35% Sb$_2$S$_3$ by Mori et al [13] has yielded 2 mm thick needles and some 5 x 10 x 0.5 mm$^3$ plates by cooling at 12°C hr$^{-1}$ from 450°C. Robertson [10] has reported the growth of single crystal pieces having the maximum dimensions 20 x 5 x 5 mm from the non-stoichiometric melt by the Stockbarger technique. It is understood from Nassau et al [11] that a run using 150 g of 40% Sb$_2$S$_3$ solution has produced a cluster of about 10 crystals 2 to 3 cm in length, the largest being 1 cm in diameter with crystal faces up to about 6 mm in width. Moreover, the detailed study of the flux growth of SbSI crystals by Bhalla et al [15] also reveals that lower cooling rate (1°C hr$^{-1}$) and a melt containing
around 38-42% Sb$_2$S$_3$ in SbI$_3$ favours the larger size crystals. From these results it is understood that bulk crystals of SbSI can be grown only by growth from the non-stoichiometric constituents at lower cooling rates.

For a number of current applications of this material in single crystal, in hot forged polycrystal [15] and in composite forms [16,17] a more detailed understanding is required of the factors controlling crystal morphology in the melt growth process, so that the size, shape and spacing of the grown crystals can be controlled to suit specific device requirements. Crystals grown with different morphologies have potential use in the field of piezoelectric and pyroelectric applications. The application of the hot forging process to a dense bundle of needles aligned parallel to the c-direction will produce a dense, well oriented polycrystal microstructure [15]. The hot forged samples are expected to have markedly improved mechanical properties and thus can be of practical use in piezoelectric hydrophone transducer application. Proper control of the needle morphology has been shown to generate regular arrays of closely spaced mutually parallel microcrystals. When these arrays are potted in an appropriate second phase they provide interesting new composite structures which have been shown to have advantageous properties for some specialized pyro- and piezo-electric applications [15].

It is a well known fact that an ingot consisting of needle crystals with their lengths (c-axes) parallel to the ingot axis can be grown from melt by vertical Bridgman technique as explained in Chapter 2. But one cannot expect dense packing of needles and perfect orientation of the needles along the ingot axis with moderate descent speeds
(moderate cooling rates). Dense packing and perfect orientation of the needles along the ingot axis can be achieved easily by the temperature fluctuation technique even with faster cooling rates. Operation of temperature fluctuations of damping amplitudes above the melting point while growing SbSI crystals from melt by the vertical normal freezing method as well as the growth habit of the crystals grown by this technique are explained in detail in this Chapter. Moreover crystals are also grown without the operation of temperature fluctuations above the melting point. The growth habits of SbSI crystals grown by these two operations are also compared and discussed.

3.2 FUNCTION OF TEMPERATURE FLUCTUATIONS

The basic idea of the use of a saw-formed alteration of temperature in the crystallization zone is that in the process of spontaneous solidification a large number of crystallization centres are formed. These centres are spontaneously oriented. The fluctuation of temperature near the melting point stimulates a growth of crystallites which are preferably oriented in the direction of heat dissipation \[18\]. In the vertical normal freezing technique the top end of the crucible containing the charge is maintained at a temperature greater than the melting point of the crystal under consideration by 50°C and the bottom end at a temperature greater than the melting point by 20° to 25°C. The radial temperature distribution across a circular cross-section of the crucible is almost uniform. In this situation the radial heat dissipation will be very small when compared to the axial heat dissipation. So the resultant heat dissipation during the growth of the crystals will be
only along the axis of the crucible. Under these circum­stances, fluctuation of temperature above the melting point will stimulate the growth of crystallites along the axis of the ingot.

According to Hintzmann et al [19] only the largest nuclei survive and grow, while the smaller ones redissolve during the peak part of the temperature fluctuation cycle. So there can be considerable reduction in the crystallization centres at the end of the temperature fluctuations. During the programmed cooling growth will occur on the small number of existing nuclei provided that the melt remains sufficiently homogeneous that further nucleation is avoided. Naturally one can expect perfect orientation of the needles along the ingot axis, close packing as well as increase in thickness of the needles from the operation of temperature fluctuations.

3.3 GROWTH OF SbSI CRYSTALS FROM MELT BY TEMPERATURE FLUCTUATION TECHNIQUE

SbSI compound synthesized from SbI₃ and Sb₂S₃ as explained in Chapter 2 is powdered well and equal amounts are taken in two identical Corning glass crucibles of 1 cm internal diameter and 10 cm length with the cone shaped small capillary at the bottom end of the crucibles to provide the site for the initial nucleation. The crucibles containing the charge are evacuated to a vacuum of 1.333 x 10⁻³ Pa and sealed off. One of the crucibles containing the charge is introduced into the vertical furnace (similar to that used for the synthesis of the compounds) and held in position so that the temperature at the initial nucleation site of the crucible is 425°C. The temperature profile of the
A furnace used is shown in Figure 3.1 [20]. When the material melts, it is kept in the molten state for few hours for homogenization by convection current and then the temperature of the nucleation site of the growth vessel is brought down from 425°C to 375°C, the supercooling temperature of SbSI [18]. The nucleation site is kept at 375°C for an hour and then its temperature is increased to 400°C, the melting point of SbSI [11]. Temperature fluctuations with decreasing amplitudes (10°C, 9°C, 8°C, 7°C, 6°C, 5°C, 4°C, 3°C, 2°C and 1°C) are then performed above the melting point. After the completion of these fluctuations, the temperature of the nucleation site of the crucible is brought down to room temperature by programmed cooling. This entire operation is shown in Figure 3.2. The rate of heating and cooling adopted throughout this process is 12°C hr⁻¹.

Operation of temperature fluctuations above the melting point has made the crystal ingot a single bundle of very closely packed parallel single crystalline needles of thickness 0.14 mm; the needles being parallel to the axis of the crucible [20]. The grown ingot is shown in Figure 3.3. Singly bundled nature of the crystal ingot can be easily understood from this figure.

3.4 CRYSTALS GROWN WITHOUT FLUCTUATIONS

The investigation is then carried out with the second crucible without temperature fluctuations. This operation is also shown in Figure 3.2 along with the previous operation for direct comparison. The growth parameters namely geometry of the crucible, composition of the charge, temperature gradient of the profile, growth process time as well as the heating and cooling rates employed are the same.
Fig. 3-1 Temperature profile of the single zone furnace
Fig. 3.2 Temperature profile with fluctuations and without fluctuations.
Fig. 3.3 SbSI ingot (single bundle)

a. grown ingot x 3.8
b. its cross-section x 6.5
c. parallel needles x 100
d. single needle x 150
as those of the previous investigation (Temperature fluctuation technique).

The crystal ingot obtained from this operation consists of many bundles of closely packed very fine needles of single crystals of SbSI. These needles are mostly oriented at random.

3.5 GROWTH OF Sb\textsubscript{0.8}S\textsubscript{0.2}I CRYSTALS FROM MELT BY TEMPERATURE FLUCTUATION TECHNIQUE

An ingot of composition Sb\textsubscript{0.8}S\textsubscript{0.2}I is also grown from melt by temperature fluctuation technique. It is grown from antimony sulfide, antimony oxide, antimony metal powder and iodine in accordance with the reaction

\[ 4 \text{Sb}_2\text{S}_3 + \text{Sb}_2\text{O}_3 + 5 \text{Sb} + 7.5 \text{I}_2 = 15 \text{SbS}_0.8\text{S}_0.2\text{I} \]  

(3.1)

4.529 g of antimony sulfide, 0.971 g of antimony oxide, 2.029 g of antimony and 6.345 g of iodine are used as the constituents of the initial charge. This charge is taken in a Corning glass crucible of 10 cm length and 1 cm internal diameter, evacuated to a vacuum of $1.333 \times 10^{-3}$ Pa and sealed. Sb\textsubscript{0.8}S\textsubscript{0.2}I ingot is also grown by operating the saw-form fluctuations above its melting point. Operation of saw-form fluctuations above the melting point is shown in Figure 3.4. The heating and cooling rates employed in this investigation is $12^\circ \text{C/hr}$.

The resultant ingot is in the form of a single bundle consisting of very closely packed single crystalline needles arranged parallel to the ingot axis \cite{21}.
Figure 3-4: Temperature profile with fluctuations.
Sb$_{0.8}$$S_{0.2}$ crystal ingot has been grown previously by Nitsche et al [22] from melt by Bridgman technique. They have also reported about the growth of an ingot consisting of densely packed single crystalline needles whose c-axes are all parallel to the ingot axis.

3.6 CONCLUSION

The operation of temperature fluctuations has not increased the thickness of SbSI as well as Sb$_{0.8}$$S_{0.2}$I needles sufficiently. But this will be possible only if the starting constituents are taken in the non-stoichiometric ratio. This is also confirmed by Nassau et al [11], Mori et al [13] and Bhalla et al [15]. Mori et al [13] have grown 2 mm thick needles as well as some 5 x 10 x 0.5 mm$^3$ plates from the non-stoichiometric melt containing 35\% Sb$_2$S$_3$ by cooling at 12°C hr$^{-1}$. Bhalla et al [15] have also reported SbSI needles of cross-section 0.1 x 0.1 mm$^2$ for 44 to 50 mole \% Sb$_2$S$_3$ and $10$-$100$°C hr$^{-1}$ cooling rate. But in the present investigation the thickness of the needles is only 0.14 mm even in the case of temperature fluctuation technique. It is understood that the thickness of the needles can be increased only by the growth from the non-stoichiometric melt with lower cooling rates. But the close packing of needles, conversion of the whole ingot into a single bundle as well as the proper orientation of all the needles being parallel to the ingot axis are the very fascinating results of the temperature fluctuation technique [20,21]. From the ingot obtained (Figure 3.3) by the temperature fluctuation technique, one can observe the very dense packing and good alignment of needles parallel to the ingot axis. This can also be achieved even by the Bridgman technique. But the major advantage of the temperature techniques...
fluctuation technique is that the growth time is very much less compared to Bridgman technique. When fast cooling rate is used in Bridgman technique, only randomly oriented needles are obtained.
LIST OF REFERENCES


