CHAPTER 4

GROWTH OF ANTIMONY CHALCOHALIDES
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4.1. INTRODUCTION

Antimony sulfo iodide and its type compounds are semi-conductors, some showing ferroelectric properties. SbSI has the highest Curie temperature among these compounds [1] and shows a displacive type ferroelectric transition at 22°C. It has interesting properties such as pyroelectric, electromechanical, electro-optic and other non-linear optical effects [2]. The other antimony chalcohalides have ferroelectric transition at low temperatures and these crystals also show photoconducting and electro-optic properties [2].

SbSI single crystals were used for light modulation [3]. SbSI based polycrystalline materials having piezoelectric properties find application as piezo-elements and transducers and are distinguished from other materials for their simplicity and their technology by reproducibility [4]. Piezo-electric elements manufactured from SbSI were operable below 20°C and piezoelectric elements doped by Sb$_2$S$_3$ were operatable up to 35°C. SbSI is also used as an IR-radiation converter, utilizing the high photosensitivity in combination with the anomalous dielectric properties in the phase transition region [5]. Single crystals of SbSI and its analogs, have been grown by a variety of methods like Bridgman, vapour phase and hydrothermal [4]. But in all the methods, needle morphology predominated with the growth rate more than 50 times parallel to C-direction than perpendicular to it.
The structure of SbSI consists of infinite sheets of composition $(Sb_2S_2I_2)$ which stretch out along the C-axis. The sheets are placed in the plane parallel to (110) face. The predominant bond in the sheet is covalent and between the sheets is Van der Waals, as a result of which there is a good cleavage along the (110) face. The structures of SbSeI, SbSBr and SbSeBr\[6\] are isomorphous with SbSI and belong to the orthorhombic system with the space group Pnam.

The (001) face of these compounds is a K-face [7] and so it grows rapidly because of the ease and independence of the joining of the structural parts by the mechanism of normal growth. A detailed experiment by Popolitov and Litvin [8] on the growth rate of SbSI crystals by hydrothermal method, showed that the activation energies for the growth of (110) and (001) faces are 8 and 2 Kcal/mole respectively.

The phase diagrams of the systems $Sb_2S_3-SbI_3$[9] (figure 4.1) $Sb_2Se_3-SbI_3$[10] (figure 4.2) $Sb_2S_3-SbBr_3$[11] and $Sb_2Se_3-SbBr_3$[12] are found to be quasi-binary. At stoichiometric compositions of antimony chalcogenide and antimony halide, the respective ternary chalcohalide is formed. SbSI and SbSeI melt congruently at 400°C and 452°C respectively. There is substantial dissociation of the melt due to the sloping liquidus in the vicinity of the compound.

4.1.2 Homogeneity of SbSI

The homogeneity range of SbSI on the $Sb_2S_3-SbI_3$ section was determined by Lazarov et al[13] from the experimental data and found that the region of SbSI homogeneity is somewhat shifted to the $Sb_2S_3$ side as shown in figure 4.3. The maximum homogeneity range was observed at 380°C and the maximum melting point
Fig. 4.1 Condensed diagram of $\text{Sb}_2\text{S}_3$–$\text{SbI}_3$ system.
Fig. 4.3
corresponds to the stoichiometric composition, which is thermodynamically stable at temperatures higher than 320°C. But there are no such reports for other antimony and bismuth chalcohalides except bismuth telluro iodide [14].

4.1.2 Thermodynamics of vapour growth

According to Aleshin et al [15], when SbSI is grown from vapour by sublimation, mass transfer of the substance via vapour is effected predominantly by diffusion of SbSI gas molecules, present in very small concentrations in the saturated vapour above the compound. It is also probable that a similar mechanism of mass transfer is realized during the crystallization of other compounds of this group. The addition of either iodine or sulphur increases the rate of mass transport during crystallization of A^V-B^{VI-C^{VII}} compounds. The chemical transport reaction responsible for these phenomena is

$$A^V B^{VI} I_s + I_2 \rightarrow A^V I_3 + \left( -\frac{1}{n} \right) B^{VI}_n$$

(4.1)

and making additional transfer of the crystalline compound by means of currents of iodine, chalcogen and metal iodide molecules. The attainment of equilibrium state is not because of the presence of iodine but also due to the incorporation of chalcogen. This is due to the fact that the system contains gaseous antimony iodide formed as a result of incongruent evaporation of the crystalline compounds

$$3A^V B^{VI} I_s \rightarrow 2A^V B^{VI}_3 + A^V I_3$$

(4.2)

and constituting the principal components of their saturated vapour [16]. It should also be noted that, according to equation 4.2,
there must be small amounts of crystalline metal chalcogenides, but these phases cannot be formed in the condensation zone due to the fact that although the transfer is in principal possible, both by sublimation and by a chemical transport reaction of the type [17].

\[
A^V_2 B^{VI}_3 + 3I_2 \rightarrow 2 A^{VI}_3 + (---) B^{VI}_{n g} \quad (4.3)
\]

Crystallization of chalcogenides is prevented by the presence of an excess pressure of the metal iodide in the condensation zone which shifts the equilibrium of equation 4.2 to the left. The authors [18] have also established that with low mass transfer rate, individual crystals grow at low supersaturations and the process rate is diffusion limited. When the mass transfer rate is high, there is bulk crystallization due to mixed diffusion kinetic conditions where the former predominates.

Growth of SbSI and its type compounds from vapour, rather than growing from melt was adopted by a number of authors, mainly due to the possibility of growing separate crystals with well defined faces. Both the sublimation and chemical vapour transport using sulphur or iodine as the transporting agent were widely used. In some cases, presynthesised SbSI was used as the starting material. In the case of crystals grown by sublimation method, both stoichiometric and excess SbI_3[19] or Sb_2S_3[20, 21] have been used.

From the literature one can observe that different authors have used ampoules of length 10-40 cm and diameter 10-40 mm for the vapour growth of SbSI type compounds. In all the cases, growth was carried out in sealed ampoules, because SbSI decomposes releasing SbI_3 when heated in air [22].
Most often, the ampoule was placed horizontally in a two zone temperature furnace. In some cases, the ampoule was inclined or even kept vertical. The temperature differences between the evaporation and condensation zones were varied from 5-10 K [23] to 150 K [24].

4.2 COMPOUND PREPARATION

The synthesis of the compounds was carried out in glass or quartz ampoules evacuated or filled with inert gas and sealed. When using elementary substances as the starting material, the process should proceed by slow heating in the initial stages so as to prevent self-heating which may be caused by the rapid progress of the reaction accompanied by a sharp rise in pressure in the ampoule; otherwise, the sharp rise in the pressure may result in explosion of the tube. SbSI can also be prepared by mixing \( \text{H}_2\text{S} \) aqueous solutions with an antimony iodide solution in HI acid [25]. SbSI and its type compounds can be prepared by three ways according to the following equations.

\[
\begin{align*}
\text{A}^\text{V} + \text{B}^\text{VI} + \text{C}^\text{VII} & \rightarrow \text{A}^\text{V} \text{B}^\text{V} \text{C}^\text{VII} \quad (4.4) \\
\text{A}_2^\text{V} \text{B}^\text{VI} + \text{A}^\text{V} \text{C}^\text{VII} & \rightarrow 3\text{A}^\text{V} \text{B}^\text{VI} \text{C}^\text{VII} \quad (4.5) \\
\text{A}^\text{V} \text{C}^\text{VII} + 2\text{A}^\text{V} + 3\text{B}^\text{VI} & \rightarrow 3\text{A}^\text{V} \text{B}^\text{VI} \text{C}^\text{VII} \quad (4.6)
\end{align*}
\]

Using the equations 4.4 and 4.5, the compounds like SbSI, SbSeI, SbTeI, SbSeBr and SbSBr were prepared by vacuum fusion. The initial elements used were antimony (99.999%), sulphur (99.999%) tellurium (99.9%), selenium (99.99%), resublimed analar grade iodine (99.9%) and bromine (99.9%). They were taken in the stoichiometric ratio in a glass ampoule of diameter 15 mm and length 20 cm. The ampoules containing elementary iodine and bromine were
heated very slowly. The temperature was kept 20 to 30°C above the melting point of each compound for 18 to 20 hours. Then it was cooled to the room temperature. Even during such a process, small needles of the respective compounds were found to have grown. The prepared material was powdered well and X-ray analysis was done using CuK radiation. The X-ray reflections for the compounds were found to agree well with the literature.

4.3 EXPERIMENTAL

4.3.1 Sublimation method.

About 5g of the polycrystalline SbSI was loaded in a glass ampoule of length 20cm and diameter 1.5cm, sealed at a pressure of $10^{-5}$ Torr and kept in a horizontal furnace. The growth zone was cleaned by initially maintaining a 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 case of SbSeI, SbSBr, and SbSeBr, 10g of the sample was taken in a glass ampoule of length 15cm and 12mm diameter with a pointed tip. For SbSeI, the source zone temperature was kept at 460°C and the growth zone temperature was varied from 380 to 440°C. For SbSBr, the source zone was kept at 280°C and the growth zone was kept at 240°C. In the case of SbSeBr, the evaporation zone was kept at 320°C and the growth zone was varied from 280 to 240°C. For SbTeI, the source zone was kept at 400°C and the growth zone was varied from 320 to 300°C.

4.3.2 Iodine transport method.

SbSI single crystals were also grown by iodine transport in a two-zone vertical furnace. About 1.0 mg of iodine per
cm$^3$ of the ampoule was used as the transporting agent in all the cases. Experiments were carried out in a sealed glass tube of length 12 cm and 10 mm diameter. The source zone temperature was varied independently.

4.4 RESULTS AND DISCUSSION.

4.4.1. SbSI- Sublimation method

Single crystals of SbSI were obtained in two days and the length was 1.0 to 15 cm and thickness ranged from 0.1 to 0.3 mm. The typical growth pattern, shown in figure 4 (plate 4.1) was obtained when the temperature difference was 20°C. In the same figure very thin needles are seen towards the end of the growth zone and thick needles proceeding the source zone. Needles of thickness 0.4 to 1.2 mm were obtained when the temperature difference was 30°C. Figures 5 and 6 (Plate 4.1) shows the brick-like elevations observed on the (110) face of the needle. This is due to the presence of stresses arising during high supersaturation. Figure 7 (Plate 4.1) represents the growth layers observed on (110) face [26].

The foreign particles arising due to the incongruent evaporation of SbSI, would be pushed away by the molecules of the growing crystal as the foreign particles enter into the crystal. There arises certain opposition and so strain arises, because the host molecules are better placed at sites than the foreign particles, as they are partially covered. This is because the impurity molecules are attracted to the incomplete layer and join on to the crystal if it is possible in any sequence with ease or there will be strain or pressure to do so. So the foreign particles are repeatedly pushed away by the growing layers. The pressure or strain may also fall when the size of the impurity molecules is of the same size of the host molecules and also when there exists large supersaturation on the growing surface. Under low
supersaturations, the impurity molecules are segregated out of the growing layers of (110) face. These molecules form a diffused layer in the vicinity of the growing steps. Hence, the front becomes tooth-like and discontinuous lines of inclusions or impurities cause stresses and the new layer inherit these stresses and if they grow under the same conditions the number of layers increases and thereby form fresh inclusions. So, more inclusions occur on these faces due to larger stresses than the subordinate faces. Sculptured shapes (figure 9 plate 4.1) develop along with the stresses. This happens in crystals growing under conditions of unequal mass transport of material supply to the growth zone[27].

4.4.2 SbTeI

Figure 10 (plate 4.2) shows the platelet of SbTeI grown when the growth zone temperature was kept at 320°C. Needles were also found to grow (figure 11, plate 4.2) when the growth zone temperature was kept at 300°C. Figures 12, 13 and 14 (plate 4.2) shows the external morphology of the grown platelets showing regular shapes. Figure 15 (plate 4.2) shows the surface of the as grown platelet, indicating spiral like patterns.

4.4.3 SbSeI

Antimony seleno iodide needles of length 10-15mm and thickness 0.5 to 1.0mm were obtained when the growth temperature was 440°C, for the growth period of 40 hours. Some needles were irregular in shape without well developed faces (figure 16, plate 4.3). With increase T, the size of the needles decreased. Figure 17 (plate 4.3) shows the higher magnification of the cleaned SbSeI needle. The respective elements in the compound were confirmed by energy dispersive spectral analysis and SEM analysis confirmed the single phase of the crystal. Crystals grown at the
growth zone temperature of 380°C, did not show any peak for selenium. In figure 18 one can observe that the selenium content decreases as the growth zone temperature decreases, and selenium separates below 380°C. Crystals grown at a temperature of 440°C show stoichiometric composition. The single crystallinity was confirmed by taking Laue photograph. The lattice parameters of the crystal for the growth zone temperature of 440°C are reported in table 4.2.

4.4.4 SbSBr

Needles of length 8 mm and thickness 0.2 to 0.5 mm were obtained when the growth zone temperature was 240°C for a growth period of nearly two days. Some of the needles show tapered ends. Figure 19 (plate 4.3) shows the platelet obtained for the growth zone temperature of 220°C grown in one week. The maximum size of the platelet obtained is 5 mm x 3 mm x 1 mm. They show (110) faces. Below 200°C, thin liquid film was observed and there was no crystallization.

4.4.5 SbSeBr

When the growth period was four days, needles of length 6-12 mm were obtained for the growth zone temperature of 280°C. The needles were of thickness 0.5 mm to 0.8 mm and the surfaces were highly reflecting. Small platelets were obtained on the walls of the tube for the growth zone temperature of 280°C. The platelets were irregular in shape and show (110) faces. The size of the platelets ranged from 4 mm x 3 mm x 0.5 mm to 5 mm x 3 mm x 1 mm. One such platelet is shown in figure 20 (plate 4.3). When the growth zone temperature was decreased, size of the needles decreased and in some cases hollow needles predominate.
ENERGY DISPERSIVE SPECTRAL ANALYSIS OF SbSeI.

Fig. 4.18
4.4.6 Iodine transport - SbSI.

Figure 21 (plate 4.4) shows the growth pattern obtained for SbSI when the temperature difference between the two zones was 40°C. In some parts of the tubes condensation of SbI₃, droplets was found. Small platelets were also found to grow, which is not observed in the case of sublimation method. When the temperature difference between the growth zone and source zone was 20°C needles of length 3 cm and thickness ranging from 0.1 to 0.5 mm were obtained near the conical tip of the ampoule. For the temperature difference of 30°C, individual needles (figures 22 and 23, Plate 4.4) not bunched together were obtained. Some of the needles were tapered as shown in Figure (Plate 4.4). Table 4.1 gives the morphology of the grown SbSI crystals [28].

TABLE 4.1
MORPHOLOGY OF SbSI GROWN BY I₂ TRANSPORT

<table>
<thead>
<tr>
<th>Ampoule dimensions</th>
<th>Temperature difference between the two zones of vertical furnace</th>
<th>Morphology and dimensions of crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>length 12 cm, diameter 10 mm</td>
<td>40°C</td>
<td>Needles length 1-3 cm thickness 0.2-1 mm; platelets (3x1x1.1 mm³)</td>
</tr>
<tr>
<td></td>
<td>30°C</td>
<td>very thin needles length 2-4 cm</td>
</tr>
<tr>
<td></td>
<td>20°C</td>
<td>Needles (some showing tapered ends) length 6-30 mm thickness 1-2 mm.</td>
</tr>
<tr>
<td>length 15 cm, diameter 12 mm</td>
<td>30°C</td>
<td>Small needles length 1-1.5 cm thickness 0.1-0.5 mm</td>
</tr>
<tr>
<td></td>
<td>40°C</td>
<td>thick needles length 2-3 cm thickness 0.8-2.5 mm</td>
</tr>
</tbody>
</table>
It has been noted that along with crystallization of SbSI a melt in the growth zone complicates the crystallization process which has been observed by many authors [19,24]. The simultaneous formation of SbSI crystals and a liquid phase in the ampoule become possible in real processes due to the sloping temperature distribution along the ampoule. The presence of insignificant excess amount of SbI$_3$ in the starting material as compared with stoichiometry, leads to the transition from VS$_{SbSI}$S$_{Sb}_2$I$_3$ to VLS$_{SbSI}$ three-phase equilibrium and the crystallization region is reduced [4]. The addition of Sb$_2$I$_3$ to stoichiometric charge induces an expansion in the crystallization region of SbSI and so the formation of SbSI takes place only under particular conditions. So, the habitus of the crystal depends on the growth conditions. When T exceeding 50°C the crystals grown do not have regular shape and are found to be hollow[29]. On increasing T in addition to condensation of the liquid the deposited crystal reveal skeletal voids, inclusions, splits and spherolitic formation [26]. The region of homogeneity of SbSI is somewhat shifted to the Sb$_2$I$_3$ side [13]. The melting point of SbSI corresponds to the stoichiometric composition which is thermodynamically stable at temperature higher than 320°C. In the present investigation, the starting material used was polycrystalline SbSI and the surface morphology is found to vary with temperature. In the case of SbSeI, below a particular temperature deficiency in selenium is observed mainly due to the incongruent evaporation of SbSeI. The other crystals SbSBr, SeTeI and SeSeBr, do not show any special features.

As mentioned, condensation observed in the growth SbSI, is due to the simultaneous formation of SbSI and liquid phase, may be SbI$_3$. Surface composition of SbSI was analysed using Electron spectroscopy for chemical analysis (ESCA) and XPS spectrum is as shown in figure 4.5. Figure 4.26 shows the thermogravimetric
Fig. 4.25 ESCA Spectrum of SbSI.
analysis (TGA) of SbSeBr Crystals. SbBr₃ was found to decompose from SbSeBr at 400°C. X-ray analysis confirmed them to be single crystals. The lattice parameters are given in table 4.2.

### TABLE 4.2

**LATTICE PARAMETERS OF ANTIMONY CHALCOHALIDES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>( ^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbSI</td>
<td>0.842</td>
<td>1.012</td>
<td>0.416</td>
<td>-</td>
</tr>
<tr>
<td>SbSBr</td>
<td>0.820</td>
<td>0.968</td>
<td>0.398</td>
<td>-</td>
</tr>
<tr>
<td>SbSeBr</td>
<td>0.831</td>
<td>1.02</td>
<td>0.394</td>
<td>-</td>
</tr>
<tr>
<td>SbSeI</td>
<td>0.867</td>
<td>1.036</td>
<td>0.414</td>
<td>-</td>
</tr>
<tr>
<td>SbTeI</td>
<td>1.37</td>
<td>0.424</td>
<td>0.920</td>
<td>128°63'</td>
</tr>
</tbody>
</table>

4. **CONCLUSION**

Single crystals of SbSI, SbSeI, SbTeI, SbSBr and SbSeBr have been grown from vapour. The observed surface features for SbSI were found to be dependent on temperature difference between the two zones. Deficiency in selenium was observed for SbSeI below a particular growth temperature and they grow as needles. Only SbSBr, SbTeI and SbSeBr were found to show platelet morphology without any special surface features.
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