CHAPTER - 2

GROWTH OF DOPED SODIUM FLUORO ANTIMONIATE CRYSTALS FROM SOLUTION

2.1 INTRODUCTION

Fluorocomplexes of sodium and ammonium are gaining interest because of their excellent properties and applications. The di-sodium penta fluoro antimonate and diammonium penta fluoroantimonate are considered important for their electro-optic and super-ionic properties (Bergman et al, 1978, Avkhutskii et al, 1983) respectively.

Gukasyan et al (1973) made extensive studies on NGR spectra on alkali metal antimony (III) fluorides, MSb$_2$F$_7$ (M = K, Na, Rb, Cs) and concluded that isometric shift $\delta$ depends upon electron density of antimony. Further they concluded that in the case of trihalides, the density of s electrons on Sb nucleus decreases with increasing differences of electronegativities and in complex fluorides of Sb(III), the unpaired pair of electrons in the valence shell of antimony is stereo chemically active.

Structure of few fluoroantimonates were discussed with the NQR study of antimony complexes (Kravchenko et al, 1974). Deformation of electron density in ammonium pentafluoro antimonate (III) crystals were reported by Makarova et al (1986). Crystal structure of thallium and ammonium tetra fluoroantimonates (III) had been reported by Ovchinniko et al (1982). Structure of ammonium penta fluoro antimonates was reported in the literature by Ryan and Cromer (1972). The
ultrasonic velocity and attenuation of phase transitions in diammonium penta fluoro antimonate crystals were reported by Samulionis et al (1987).

X-ray analysis of Na$_2$SbF$_5$ (Habibi at al 1974) and Na$_2$Sb$_3$F$_{10}$ (Ducourant et al 1975); Crystal structure of MSb$_3$F$_{10}$ ($M = NH_4$, Rb, Tl) (Ducourant et al 1983); X-ray studies of thermal expansion and phase transition in diammonium fluoro antimonate (III) (Waskowska et al 1990) are the literature report available for X-ray analysis for the crystals of fluoro complexes. Crystal structure evaluation on ammonium pentafluoroantimonate (III) by Ryan and Cromer (1972); studies on the formation of four complexes of composition Cs$_2$SbF$_5$, CsSbF$_4$, CsSb$_2$F$_{13}$, CsSb$_2$F$_7$ (Zimina et al 1975); formation of five complexes Rb$_2$SbF$_4$, RbSbF$_4$, RbSb$_2$F$_7$, RbSb$_3$F$_{10}$, RbSb$_4$F$_{13}$ (Zimina et al 1976); structural evaluation of the compounds MSb$_2$F$_7$ ($M = K$, Rb, Cs, NH$_4$, Tl) by Habibi et al (1974); structure analysis in AF - BF$_3$ systems ($A = K$, Rb, Cs, Tl; $B = A1$, Fe, Cr, Ga, V, Tl, Ln) by Carl Pistorius (1975) had been cited as important work on fluoroantimonates.

The Mössbauer spectra of RSb$_2$F$_7$ ($R = Na, K$) (Birchall and Dellavalle 1971); Mössbauer studies of (NH$_4$)$_2$SbF$_5$ (Gorkov and Davidovich 1975) and on NH$_4$Sb$_3$F$_{10}$ (Ballard et al 1976) had been realised in the literature.

The EPR studies on the charge compensation effects in manganese (II) doped (NH$_4$)$_2$SbF$_5$ was reported by Prasad and Sreeramachandra Subramanian (1986). ESR spectra of Mn$^{2+}$ doped (NH$_4$)$_2$SbF$_5$ crystals had been carried out Trifimov et al (1990). Moskvich et al (1989) reported the electrical conductivity studies on isostructural polycrystalline penta fluoro antimonate M$_2$SbF$_5$ ($M = Rb, K, Cs, Tl, NH_4$) and concluded that these compounds have high conductivity at high temperatures amounting to $1 - 10 \ \Omega^{-1} \ \text{m}^{-1}$ in the case of thallium and
ammonium salts, typical of superionic crystals. The temperature dependence of proton relaxation study in (NH₄)₂SbF₅ in the temperature range 230 - 400 K shows a peak at 257 K (Bandyopadhyya et al 1989). The NQR studies in the temperature range 77 - 380 K and IR studies in the range 130-325 K were carried out on MSbF₄ (M = Na, K, NH₄, CN₃H₆) by Zemnukhova et al (1986). NQR studies of phase transitions and intermolecular interactions in (NH₄)₂SbF₅ showed unusual positive temperature coefficients of Sb resonance frequencies below the phase transition at 169 K (Nakamura and Nobuo 1986).

The growth of single crystals of orthorhombic NaBF₄ of optical quality with dimensions upto 30 x 30 x 40 mm³ have been grown from aqueous solutions by controlled evaporation at constant temperature and the measurement of dielectric constants, indices of refraction, coefficients of thermal expansion, elastic, thermoelastic and piezoelectric constants were reported by Gnanam et al (1986).

The crystal growth and physical properties of monoclinic betaine fluoroborate monohydrate (CH₃)₃NCH₂COOHBF₄·H₂O has been reported by Wang Jiyang et al (1986) and physical properties such as dielectric constant, coefficient of thermal expansion, index of refraction, elastic and thermoelectric constants were carried out by them.

Radiation induced paramagnetic defect centres in NaBF₄ crystals (Pattern 1973) were reported in the literature.

The literature report of crystal data of sodium fluoroantimonates is reported in Table 2.1. The index of refraction of Na₂SbF₅ crystals and the nonlinear optical results of Na₂SbF₅ according to Bergman et al (1978) are reported in Table 2.2 and Table 2.3.
Table 2.1

Crystal data of sodium fluoroantimonates

<table>
<thead>
<tr>
<th>Crystal</th>
<th>System</th>
<th>Space group</th>
<th>Crystal Parameters</th>
</tr>
</thead>
</table>
| NaSbF<sub>4</sub> | Monoclinic  | P<sub>21/a</sub> or P<sub>21/c</sub> (C<sub>2h</sub><sup>5</sup>) | a = 08.5749 Å  
                |                |                   | b = 05.5299 Å  
                |                |                   | c = 08.0703 Å  |
| Na<sub>2</sub>SbF<sub>5</sub> | Orthorhombic | P<sub>212121</sub> (D<sub>2</sub>) | a = 05.439 Å  
                |                |                   | b = 11.110 Å  
                |                |                   | c = 08.065 Å  |

Table 2.2

Index of refraction of Na<sub>2</sub>SbF<sub>5</sub>

<table>
<thead>
<tr>
<th>Index of refraction</th>
<th>0.53 μm</th>
<th>1.06 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>n&lt;sub&gt;x&lt;/sub&gt;</td>
<td>1.474</td>
<td>1.449</td>
</tr>
<tr>
<td>n&lt;sub&gt;y&lt;/sub&gt;</td>
<td>1.479</td>
<td>1.467</td>
</tr>
<tr>
<td>n&lt;sub&gt;z&lt;/sub&gt;</td>
<td>1.438</td>
<td>1.426</td>
</tr>
</tbody>
</table>
Table 2.3

Non-linear optical result, d values and coherence length (l's) of Na$_2$SbF$_5$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{123}$</td>
<td>$2.9 \times 10^{-10}$ esu</td>
</tr>
<tr>
<td>$\frac{1}{2}(d_{231} + d_{312})$</td>
<td>$2.6 \times 10^{-10}$ esu</td>
</tr>
<tr>
<td>$l_{123}$</td>
<td>9.4 $\mu$m</td>
</tr>
<tr>
<td>$l_{231, 312}$</td>
<td>26.2 $\mu$m</td>
</tr>
</tbody>
</table>
Since no attention was so far paid on doped crystals of sodium fluoroantimonates these crystals are grown with doping different amounts of fluorides (BaF$_2$, AlF$_3$) having ionic radii comparable to Na$^+$ ions. Physical properties like electrical conductivity, dielectric constant, microhardness measurements, and surface characteristics (chemical etching), thermal analysis (DSC, TG), X-ray studies and spectroscopic characterisation (IR, LR) are studied in this volume of work.

2.2 EXPERIMENTAL

2.2.1 Preparation of the material

Antimony trifluoride and sodium fluoride form many stoichiometric compounds. Antimony trifluoride is obtained by reacting Sb$_2$O$_3$ with HF (48%) in the appropriate molar ratio according to the chemical equation

$$\text{Sb}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{SbF}_3 + 3\text{H}_2\text{O} \quad (2.1)$$

Antimony trifluoride is reacted with sodium fluoride in the appropriate molar ratio. The equations are given below.

$$\text{SbF}_3 + \text{NaF} \rightarrow \text{NaSbF}_4 \quad (2.2)$$
$$\text{SbF}_3 + 2\text{NaF} \rightarrow \text{Na}_2\text{SbF}_5 \quad (2.3)$$

To the prepared solution of NaSbF$_4$ and Na$_2$SbF$_5$, barium fluoride and aluminium fluoride are added in 500, 750, 1000 ppm levels in solution form. The pH of the solution is 8.2 and 8.7. Thus the mother solution for all materials are obtained. Above reactions are carried out in polyethylene containers. The solution is stirred for few hours using magnetic stirrer with teflon coated paddle to ensure completion of the reaction. The solution is then concentrated in a hot water bath to
obtain supersaturation. On cooling, recrystallization of the compound takes place from the supersaturated solution.

2.2.2 Seed preparation

The solution of the compound is allowed to supersaturate under controlled evaporation of the solvent. Spontaneous nucleation occurs and the crystals of considerable size are allowed to grow at the bottom and side walls of the container. Most of the crystals are highly transparent crystals. The crystals of optimum size crystals of length 5 to 10 mm with edges clearly defined are picked out and examined under a microscope. Highly transparent crystals are used as seed crystals for growing large size single crystals.

2.2.3 Growth experiment

Constant temperature bath with necessary heaters, controllers and temperature measuring devices are required for crystal growth by slow evaporation technique. The bath liquid is heated to the desired temperature using two immersion heater coils. The power input to the heating coils is controlled by relay setup so that bath temperature is maintained at the set temperature with an accuracy of ± 0.01°C. The temperature gradient with in the bath is avoided by constant stirring. The growth temperature is maintained as 305 K. In order to obtain saturated solution, an excess amount of material and water are taken in a PVC container and the solution is stirred well for few days. Thus a saturated solution at that temperature is obtained. The saturated solution is transferred to another beaker and warmed five degrees above the bath temperature. This process helps to dissolve tiny crystallites if any present in the solution. By this process, the solution becomes slightly under-saturated. When the solution temperature reaches two degrees above the bath temperature, the solution is transferred into the growth
vessel containing the seed crystals fixed at the bottom of the vessel. The growth vessel is transferred to the constant temperature bath and the solution remain undisturbed and not stirred for 12 hours. Since the solution is just undersaturated at the time of transfer of the solution and there is no stirring, the seed slightly dissolves and the dissolved material of the seed forms a layer of higher concentration around the surface of the seed crystal. This will prevent further dissolution of the growing crystal. The dissolution stops when the temperature of the solution reaches the temperature of the bath. After 12 hours the solution is stirred using a stirrer at about 200 r.p.m. The diffuse layer surrounding the crystal surface is reduced to zero thickness and uniform concentration is maintained at every point in the solution by constant stirring. When slow evaporation occurs the solution becomes slightly supersaturated and this supersaturation becomes the driving force for the growth of the crystals. The crystals are harvested when they attain optimum size. The powder diffraction patterns of doped crystals of NaSbF₄, Na₂SbF₅ were recorded with Reich-seiferet 3000p with monochromatic nickel filtered CuKα having wavelength λ = 0.15406 nm as the source. The samples were scanned from 10 to 75°. The input voltage and current are 35 kilovolt and 30 mA. Thus the powder diffraction data has obtained for all compounds and d and hkl values are compared with the literature values.

2.3 RESULTS AND DISCUSSION

Figs 2.1 and 2.2 show Ba²⁺ and Al³⁺ doped crystals of NaSbF₄ in three different concentrations. Similarly Figs. 2.3 and 2.4 show the Ba²⁺ and Al³⁺ doped crystals of Na₂SbF₅ in three concentrations. From the results of Inductively Coupled Plasma (ICP) technique, it is found that the actual amount of dopant deliberately added is not exactly equal to the amount of dopant present in the lattice. Undoped crystals (Bennet Charles 1992) of NaSbF₄ crystal size
Figure 2.1  (a) Ba 55  
(b) Ba 60  
(c) Ba 66

Figure 2.2  (a) Al 130  
(b) Al 148  
(c) Al 172
Figure 2.3 (a) Ba 66
(b) Ba 71
(c) Ba 79

Figure 2.4 (a) Al 120
(b) Al 135
(c) Al 148
45 × 40 × 20 mm$^3$ were obtained in a period of 5 months and N:
dimension of 22 × 35 × 18 mm$^3$ were obtained in 8 months. Compar-
doped crystals with that of the undoped crystals for the same gro-
size of the doped crystals are smaller. Size of the crystals are tabu-
This is due to the fact that the impurities reduce the growth rate. Sim-
main for Na$_2$SbF$_5$ crystals also. Sagayaraj (1995) have also stud-
growth rate of PbBr$_2$ due to the presence of barium impurity. Lan-
(1996) studied the defect structure of manganese doped barium tit-
BaTi$_{1−x}$Mn$_x$O$_3$ in the region 0 ≤ x ≤ 0.05 and reported the drast-
growth rate. Regarding the optical transparency, there is no at-
significant change between doped and undoped samples as obser-
In order to con.... crystals EDS (Ener-
Spectroscopy) was carried out and confirmed the existence of maj-
and chemical composition. Figs. 2.5 and 2.6 shows the EDS spect-
doped crystals of NaSbF$_4$ and Na$_2$SbF$_5$. For confirming minor co-
are deliberately added during growth, the Inductively coupled pla-
(ICP) is carried out on these samples. Table 2.4 shows the amc-
components present in the crystals.

The Laue patterns of the above said crystals are recorded i-
in Figs. 2.7 and 2.8.
Table 2.4

The ICP report and crystal size of doped NaSbF₄ and Na₂S

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Dopant</th>
<th>Dopant added during growth in ppm</th>
<th>Dopant concentration as per ICP report</th>
<th>Cr S in</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSbF₄</td>
<td>Ba</td>
<td>500</td>
<td>55</td>
<td>23 x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>750</td>
<td>60</td>
<td>30 x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>68</td>
<td>20 x</td>
</tr>
<tr>
<td>NaSbF₄</td>
<td>Al</td>
<td>500</td>
<td>130</td>
<td>16 x (</td>
</tr>
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</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>148</td>
<td>30 x 1</td>
</tr>
</tbody>
</table>
2.4 CONCLUSION

Barium and aluminium doped crystals of NaSbF$_4$ and Na$_2$SbF$_5$ are grown. The growth period was about six months. EDS spectra has been taken to confirm the major components present and ICP studies have been carried out to get the amount of minor components present. Transparency has not been affected by doping. Finally it is concluded that the deliberate addition of impurities decrease the growth rate.