CHAPTER 5

GROWTH OF SnI$_2$ AND SnI$_4$ SINGLE CRYSTALS IN SILICA GELS

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5.1 Introduction

The gel method has proved beyond doubt a promising technique for growing single crystals, especially of inorganic materials insoluble and sparing soluble in water and which cannot be conveniently grown from melt or from the vapour\(^1\). It has been reported\(^2\) that a variety of crystals suitable for research and technology can be grown in silica gel. Gels can act as excellent supporting media (for growth of crystal) through which the reacting materials can diffuse at a rate conductive for growth of crystal to proceed. Crystals grown by gel technique are normally well faceted and show many crystallographic features.
Research in this field has progressed by leaps and bounds with the pioneering work of Henisch et al.\textsuperscript{5)}

The growth of single crystals of tin-iodides is of considerable interest particularly for basic studies of their electric, optical and other pertinent characteristics\textsuperscript{6-7}). The importance of gel technique and its preference to other crystal growth techniques have been emphasized in chapter 1. In this chapter the performance and potentiality of the gel technique is tested in producing larger and more perfect single crystals of SnI\textsubscript{2} and SnI\textsubscript{4}, the two different phases in the same experimental set up.

5.2 Experimental and Observations

5.2.1 Preparation of silica gel

The diluted solution of commercial water glass was centrifuged at 15000 rpm to separate the floating and suspended impurities. As a result transparent golden coloured solution of sodium meta silicate was obtained and could be preserved as a stock solution for quite a long time. To this sodium meta silicate solution was added a required quantity of doubledistilled water to give a resulting solution of specific gravity 1.03-1.06. When the solution of sodium meta silicate is mixed with
any mineral or organic acid, gel formation takes place due to polymerization as described in chapter 1. Time required for gelation depends on density and pH of gel solution, acid used for gelation and temperature. Gels of low density and low pH values required relatively longer time for setting.

In the present work the stannous chloride (SnCl₂·2H₂O) solution was prepared by dissolving it in an appropriate amount of concentrated hydrochloric acid to prevent hydrolysis and then diluted to the required strength. Freshly prepared solution was used to avoid the possibility of oxidation. Gels were prepared by mixing sodium meta silicate solution with this stannous chloride solution. It was found that even a very small change in amount of stannous chloride solution used, changes in pH were of very large magnitudes. This is because the stannous chloride solution contains concentrated hydrochloric acid, which is a very strong acid compared to organic acids. This demands great vigilance in deciding the amount of stannous chloride solution to be used in order to secure appropriate range of pH values which in turn gives a good gel.

5.2.2 Crystal growth

The various crystallization apparatus used
in the present investigation are (i) 250 ml beakers and (ii) standard test tubes of 2 to 3.5 cm diameter and 25 cm long. The technique of incorporating one reagent in a gelling mixture, while another is later on diffused into the gel, leading to very high supersaturation and in due course to initiate nucleation and crystal growth is used. Silica gels were prepared by mixing sodium-meta-silicate solution (sp.gr. 1.04) with 10 N stannous chloride HCl solution. The optimum value of pH of resulting solution was found to be approximately 3. The chemicals used are (i) B.D.H. AnalaR HCl (35.47 %), (ii) Extra pure SnCl₂.2H₂O (97.07 %) and (iii) Extra pure KI (99.5 %). In order to grow SnI₂ and SnI₄ crystals in gel medium, the following reaction have been employed.

\[ \text{SnCl}_2 + 2\text{KI} \rightarrow \text{SnI}_2 + 2\text{KCl} \quad (5.1) \]

In presence of concentrated hydrochloric acid, KI liberated iodine ions, then the following reaction takes place:

\[ \text{KI} + \text{HCl} \rightarrow \text{KCl} + \text{H}^+ + \text{I}^- \quad (5.2) \]

\[ \text{Sn}^{++} + \text{I}^- \rightarrow \text{Sn}^{+++] \quad (5.3) \]
or \[ \text{SnI}_2 + 2\text{I}^- + 0 + 2\text{H}^+ \rightarrow \text{SnI}_4 + \text{H}_2\text{O} \quad \ldots \ (5.4) \]

The gel pH of approximate value 3, was usually found to set within 2-3 days, depending on the environmental temperature. After ensuring proper gel setting, the growth experimenta was started by adding the feed solution, KI of varying strength from 0.5 N to 2.0 N, above the gel set with the help of a pippette, the drops from the pippette being allowed to a fall along the sides of the test tube in order to prevent breaking of surface and inner structure. On adding KI as supernatant solution, it was found that a yellow precipitate is formed at the gel solution interface.

Following the 250 ml beaker system, it was observed that for a concentration of KI, 1.0 N or above, yellow long needles of SnI$_2$ were formed at the gel solution interface, while the nucleation of SnI$_4$ crystals started below the interface (fig. 5.1). Completion of crystallization of SnI$_2$ and SnI$_4$ crystals took about 15-20 days. Though there would be a greater degree of freedom for lateral diffusion in this system, the large number of nucleation sites impede the size of growing crystals.
In test tube system, it was observed that, for concentration of the KI solution of less than 1.0 N, only yellowish needles of SnI$_2$ crystals were obtained while at a concentration of 1.0 N KI solution, both needles of SnI$_2$ crystals and orange to reddish SnI$_4$ crystals were obtained (fig. 5.2). At higher concentration of KI solution large single crystals of SnI$_4$ alone were produced. With further increase in the concentration to nearly 2.0 N, SnI$_2$ whisker were obtained. Figures 5.3(a-d) show the growth of SnI$_2$, SnI$_4$, SnI$_4$ and SnI$_2$ whiskers, respectively in the gel medium. It is observed that in this system, the crystals that grew were less in number and more perfect with increasing distance from the gel interfaces. This may be explained as due to slow diffusion of KI solution into the gel medium. The experimental details and growth parameters are summarised in table 5.1. The results are based on the statistical average of five sets of experiments. From table 5.1, it is clearly seen that the growth rate of SnI$_2$ crystals is greater than that of SnI$_4$ crystals.

5.2.3 Morphology

Figures 5.4(a) and 5.4(b) show some typical crystals of SnI$_2$ and SnI$_4$ grown in the present
**Table 5.1 Growth parameters for growing SnI₂ and SnI₄ crystals**

<table>
<thead>
<tr>
<th>Concentration of SnCl₂ sol.</th>
<th>Concentration of KI sol.</th>
<th>Compound incorporated with gel set(N)</th>
<th>Size of grown crystals (mm)</th>
<th>Period in days</th>
<th>Habit of the grown crystals</th>
<th>Quality of the crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 SnI₂</td>
<td></td>
<td></td>
<td>4</td>
<td>7</td>
<td>Needles</td>
<td>Transparent</td>
</tr>
<tr>
<td>1.0 SnI₂</td>
<td></td>
<td></td>
<td>7</td>
<td>5</td>
<td>Needles</td>
<td>Transparent</td>
</tr>
<tr>
<td>0.5 SnI₂ and SnI₄</td>
<td></td>
<td></td>
<td>2</td>
<td>28</td>
<td>Octahedral</td>
<td>Transparent</td>
</tr>
<tr>
<td>1.5 SnI₂ and SnI₄</td>
<td></td>
<td></td>
<td>2</td>
<td>21-28</td>
<td>Octahedral</td>
<td>Transparent</td>
</tr>
<tr>
<td>2.0 SnI₂ and SnI₄ whisker</td>
<td></td>
<td></td>
<td>10</td>
<td>6</td>
<td>Octahedral, rod-like, platelet and prismatic.</td>
<td>Transparent</td>
</tr>
<tr>
<td>0.5 SnI₂</td>
<td></td>
<td></td>
<td>9</td>
<td>5</td>
<td>Needle, rod-like, platelet and prismatic.</td>
<td>Transparent</td>
</tr>
<tr>
<td>1.0 SnI₂ and SnI₄ whisker</td>
<td></td>
<td></td>
<td>9</td>
<td>5</td>
<td>Needle, rod-like, platelet and prismatic.</td>
<td>Transparent</td>
</tr>
<tr>
<td>1.0 SnI₂</td>
<td></td>
<td></td>
<td>9</td>
<td>21-28</td>
<td>Octahedral with {100}, {110} and {210}</td>
<td>Transparent</td>
</tr>
<tr>
<td>1.5 SnI₂ and SnI₄ whisker</td>
<td></td>
<td></td>
<td>10</td>
<td>4-6</td>
<td>Octahedral with {100}, {110}, {210}</td>
<td>Transparent</td>
</tr>
<tr>
<td>1.5 SnI₂</td>
<td></td>
<td></td>
<td>3-4</td>
<td>21-28</td>
<td>Octahedral</td>
<td>Transparent</td>
</tr>
<tr>
<td>2.0 SnI₂ and SnI₄ whisker</td>
<td></td>
<td></td>
<td>3-4</td>
<td>21-28</td>
<td>Octahedral</td>
<td>Transparent</td>
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<tr>
<td>2.0 SnI₂ and SnI₄ whisker</td>
<td></td>
<td></td>
<td>10</td>
<td>4</td>
<td>Octahedral</td>
<td>Transparent</td>
</tr>
</tbody>
</table>
work. The SnI_2 and SnI_4 crystals are usually long yellowish needles and red octahedrals respectively. With the help of X-ray rotation photograph (chapter 8) the orientation of needle was found to be 010.

It is observed that a change in concentration of feed solution (KI) has a remarkable effect on the crystal morphology. At 1.0 N concentration of feed solutions, the SnI_2 crystals in the habit of rod-like and prismatic were found to grow as shown in fig. 5.5(a). The development of different habits is schematically shown in fig. 5.5(b). It is clearly seen from fig. 5.3(b) that the smaller crystals of SnI_4 are more transparent and well defined, implying thereby that the crystal quality deteriorates with an increase in size. At concentrations of 1.0 N of both the solutions almost all crystals were grown in perfect octahedron form bounded by {111} faces and at higher concentrations of 1.5 N of either solutions, the other faces {100}, {110} and {210} were subordinated to {111} faces as shown in fig. 5.6(a). The development of different faces is schematically shown in fig. 5.6(b).

5.3 Discussion

According to reaction (5.1) single crystals of
SnI₂ correspond to the primary product obtained, and later when iodine ions are liberated from KI solution, in presence of concentrated hydrochloric acid, SnI₄ crystals are formed according to equations (5.3) and (5.4). The lower concentrations of KI solution favoured the growth of only SnI₂ crystals while higher concentrations of KI solutions yielded SnI₄ crystal, as more iodine would be available for oxidising Sn⁺⁺ to Sn⁴⁺⁺. But at a critical concentration of KI solution, (1.0 N), both SnI₂ and SnI₄ have been grown together in the same experimental set up. It has been observed that at a very high concentration of KI solution (2.0 N), the whiskers of SnI₂ crystal are produced due to fast growth at higher supersaturation. The details of whisker growth and morphology are dealt in chapter 9.

Different habits of crystals in different regions of the growth medium may be attributed to different concentration gradients and growth rates. In the present investigation lamellar and prismatic needles and rod like platelet needle of SnI₂ are found to grow in regions of higher concentration gradients. Away from the gel interface, rate of diffusion of the feed solution gradually reduces in gel, and when it becomes steady, well
developed prismatic and rod-like platelet transparent needles of SnI₂ and transparent, red octahedral crystals of SnI₄ result. It is observed that the reaction waste product has a remarkable effect on size and quality of the crystals. It is likely that the translucency of large crystals of SnI₄ is due to incorporation of reaction waste product.

5.4 Conclusions

1. Single crystals of two different phases, SnI₂ and SnI₄ have been grown in the same experimental set up in silica gels.

2. Transparent bright yellowish needles of SnI₂ upto 9 mm and orange to reddish octahedral SnI₄ crystals upto 3-4 mm have been obtained.

3. The growth rate for SnI₂ crystals is found to be faster than that of SnI₄ crystals.

4. By changing the concentrations of feed solutions, crystals with different morphologies have been obtained.

5. The waste product of reaction affects the size and transparency of the growing crystals.
References


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"Crystal Growth in Gels"

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6. Zollweg, R. J. and Frost, I. S.

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Captions of the figures

Fig. 5.1 Schematic representation of growth of SnI₂ and SnI₄ crystals in silica gel in a beaker.

Fig. 5.2 Schematic representation of growth of SnI₂ and SnI₄ crystals in silica gel in test tube.

Fig. 5.3(a) SnI₂ crystals growing in silica gel.

Fig. 5.3(b) SnI₂ and SnI₄ crystals growing together in silica gel.

Fig. 5.3(c) SnI₄ crystals growing in silica gel.

Fig. 5.3(d) SnI₂ whiskers growing in silica gel.

Fig. 5.4(a) Some of the typical crystals of SnI₂ grown in silica gel, mm scale.

Fig. 5.4(b) Some of the typical crystals of SnI₄ grown in silica gel, mm scale.

Fig. 5.5(a) Development of different habits such as needles, rod-like and prismatic SnI₂ crystals.

Fig. 5.5(b) Schematic representation of different habits of SnI₂ crystals: a, b, c, r and n are \{100\}, \{010\}, \{001\}, \{101\} and \{111\}.

Fig. 5.6(a) Development of different habits of SnI₄ crystals.

Fig. 5.6(b) Schematic representation of different habits of SnI₄ crystals and a, c, d and e are \{100\}, \{111\}, \{110\} and \{210\}. 