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## **CHAPTER – III**

**GROWTH OF SINGLE CRYSTALS OF  $\text{CaSO}_3$   
IN SILICA GEL**

## CHAPTER 3

### GROWTH OF SINGLE CRYSTAL IN GELS

#### 3.1 Introduction:

Growth of single crystals in gels has received considerable importance because this method is particularly useful to grow single crystals of substances which are insoluble in water and which cannot be conveniently grown from the melt or from the Vapour. The gel medium prevents turbulence, acts as a catalyst, and permits the electrolytes to diffuse at a desirable controlled rates. Eventhough crystals of a large number of materials including semiconductors [1,2,3,4], ferroelctrics [5,6,7], metals [8,9] and highly water-soluble substances such as KDP [10,11] and ADP [12] have been grown, growth of calcium sulfite crystals has been of great interest in this laboratory [13].

Very small single crystals of size upto  $0.4 \times 0.04 \times 0.005$  mm<sup>3</sup> of calcium sulfite have been grown from aqueous solutions for X-ray studies [14,15,16] have grown spherulites ( $\approx 0.5$  mm) and single crystals (size  $\approx 50$   $\mu$ m) of CaSO<sub>3</sub> using agar-agar gels. We found that the crystals grown in agar-agar gel are not transparent and well defined. Therefore, we have used silica gels and the present chapter deals with the successful growth of larger and good quality CaSO<sub>3</sub> single crystals in silica gel.

### 3.2 Experimental Procedures:

The controlled chemical reaction between two soluble components diffusing through the gel was used for the crystal growth. The silica gel (acidified sodium meta silicate) was used as the growth media throughout this study.

The crystallization apparatus used in the present work were (i) 250 ml beaker, (ii) U-tubes of 2.5 to 4 cm diameter and (iii) test-tubes of size 25 mm outer diameter and 200 mm length.

Sodium metasilicate stock solution was prepared in the following way: two kilograms of sodium metasilicate powder (Romali Company, Austria) dissolved in four litres of double distilled water. This solution was stored for several months, so that most of the heavy impurities were settled at the bottom of the container. Finally, the solution was centrifuged and then we obtained very clear solution of sodium metasilicate.

To the sodium metasilicate was added the required amount of distilled water to give a resulting solution of specific gravity of 1.04, to which the required quantity of 1 or 2 N acetic acid was added drop by drop with constant stirring to form the gel.

The following chemical reaction was employed which took place in the gel medium:



The chemicals used for growing these crystals were: (i) Loba "G.R."  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_3$  and (ii) B.D.H. "Anala R"  $\text{CH}_3\text{COOH}$ .

Following the beaker system, the gel solutions were prepared by mixing 1 or 2 N acetic acid with 1.4 sp.gr. sodium metasilicate solution. To this mixture, one of the reactants, either  $\text{CaCl}_2$  or  $\text{Na}_2\text{SO}_3$  solution of concentration varying from 0.1 to 1 N was added. Preparation of gel solutions was found to be very critical because of the reaction of the reactants with sodium metasilicate. Therefore, first we have brought down the pH of the gel solution to around 4 by adding the required amount of 1 N acetic acid. Then only, one of the reactants was added to the gel forming solution. It has been found that the gel solutions of pH values greater than 8 resulted in immediate precipitation when one of the reactants was added. Therefore, we have chosen gel solutions with pH values always below 6.

After setting the gels, (gelation time varied between 12 hours and 2 days depending on the amount and concentration of  $\text{CH}_3\text{COOH}$ ), the second reactant (either  $\text{CaCl}_2$  or  $\text{Na}_2\text{SO}_3$ ) was added on the top of the gel. The concentration of the feed solutions varied from 0.1 to 1.5 N. It was observed that when the concentrations of more than 1 N of feed solutions were used, the density of nucleation centres tremendously increased. The nucleation started only on the solution-gel interface for concentration of feed solutions upto 0.4 N,

but for higher concentrations crystals formed just below the interface. This procedure yielded good single crystals upto  $3 \times 2 \times 1.5 \text{ mm}^3$  size. The growth period was about 6 weeks.

In the second method, using U-tubes [13] of different diameters varying from 2.5 to 5 cm, the neutral gels were prepared by mixing 1.04N sodium silicate and 1 to 2 N acetic acid solutions. After setting the gels, the feed solutions of  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_3$  of concentrations varying from 1 to 2 N were added in the two limbs of the U-tube and the crystals were allowed to grow. This method produced good single crystals of  $5 \times 3 \times 2 \text{ mm}^3$  size and it took eight weeks to obtain crystals of this size.

In the third method, instead of the beaker, test tubes of different diameters varying from 2 to 5 cm were used. The gels were prepared in the same way as in the case of the beaker system. The concentration of the feed solutions was varied from 0.1 to 1 M. It was verified that crystals formed in large diameter tubes were generally larger than those found in smaller diameter ones. In this system, the crystals that grew were less in number and more perfect with the increasing distance from the gel-solution interface. Since the crystals are soluble in the reaction waste products, the small nuclei at the beginning of growth might dissolve and thus reduce the density of nucleation. This will in turn reduce competition for solute [17], leading to larger crystals. It is observed that

the crystals at greater depths from the gel-solution interface, in the gel grow more slowly, less in number and are more transparent because of the smaller concentrations gradients than those near the top. Because of slow diffusion, test tube method yielded the best quality single crystals, in terms of transparency and inter-crystalline separation, upto  $10 \times 5 \times 3 \text{ mm}^3$  size. A few of the growth crystals of  $\text{CaSO}_3$  are shown in Fig.1

### 3.3 Characterization:

The crystals were identified as  $\text{CaSO}_3 \cdot 0.5 \text{ H}_2\text{O}$  with X-ray powder diffraction method. X-ray diffraction powder pattern confirmed the crystal structure to be orthorhombic. The calculated lattice parameters are  $a = 9.808 \text{ \AA}$ ,  $b = 10.676 \text{ \AA}$  and  $c = 6.496 \text{ \AA}$ , which agree well with the values reported in the literature [18]. The data of powder diffraction pattern shown in Table-1 was in good agreement with the data reported in [19]. The X-ray oscillation photograph taken along C-axis shown in Fig. 2, clearly indicates from the sharp spot pattern, that the  $\text{CaSO}_3$  crystals are perfect single crystals. The density of the crystals was measured by the flotation method and was found to be  $2.52 \text{ gm/cm}^3$ .

### 3.4 Morphology:

Fig. 1 shows some typical crystals of  $\text{CaSO}_3$  grown in the present work. It is observed that the smaller crystals are more transparent and

well defined compared to larger crystals, implying thereby that the crystal quality deteriorates with the increase in size.

It is observed that the incorporation of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) solution with the gel forming solution resulted into only spherulites (Fig.3) whereas incorporation of calcium chloride ( $\text{CaCl}_2$ ) solution with the gel solution gave good quality single crystals (Fig. 4), after one month of growth period. In the case of  $\text{CaCl}_2$  incorporated gels, precipitation started as soon as the feed solution of  $\text{Na}_2\text{SO}_3$  added (from 0.1 to 1 M). The precipitation depth from the gel-solution interface varied from 1 mm to 2 cm distance. Below precipitation, spherulites and dendrites followed by single crystals have been observed as shown schematically in Fig. 5. In the  $\text{CaCl}_2$  electrolyte incorporated gels, after 2 months of growth period all the dendrites and spherulites got converted into needles (at the top of the gel) and single crystals (below the needles as shown in Fig. 6). The conversion of early formed spherulites and dendrites into needle and single bulk crystals was observed in most of the cases of low pH ( $\approx 4$  to 5) gels.

### 3.5 Discussion:

It has been reported in the literature that in gels, the growing crystals either displace [20] or trap the gel [21] as they grow. In the present case, we have observed cusps around the growing crystals which indicates that the crystals were grown by the displacement of gel. It is observed that low pH gels (below 5)

with  $\text{CaCl}_2$  solution incorporated gels gave good quality single crystals compared to  $\text{Na}_2\text{SO}_3$  solution incorporated gels which may be due to the excess incorporation of sodium ions into the growing crystals, in the latter case. This may also be due to the larger molecular weight of  $\text{Na}_2\text{SO}_3$  molecules compared to  $\text{CaCl}_2$  molecules. The formation of precipitate and dendrites near the gel-solution interface is due to the fact that near the gel-solution interface the reaction rate is faster compared to higher depths in the gel. The crystals formed below the dendrites will grow more slowly than those near the top, because of smaller concentration gradients and hence the crystals formed at greater depths are more well defined. The conversion of early formed precipitate, spherulites and dendrites into single crystal needles and bulk crystals is due to the fact that the dissolution of  $\text{CaSO}_3$  material in  $\text{Na}_2\text{SO}_3$  feed solution followed by crystallization in gel. This fact has been confirmed by measuring the solubility of  $\text{CaSO}_3$  material in  $\text{Na}_2\text{SO}_3$  solution, which has been found to be around 0.5 gm/100 ml of 0.5M  $\text{Na}_2\text{SO}_3$ . These experimental results have been confirmed during the growth of these crystals in the tubes. In the case of U-tube method, in the gel nearer to  $\text{CaCl}_2$  feed solution hundreds of nucleation centres were formed whereas in the gel nearer  $\text{Na}_2\text{SO}_3$  feed solution only a few crystals were formed as shown schematically in Fig. 7.

### 3.6 Conclusions

- 1 Single crystals of calcium sulfite upto  $6 \times 5 \times 3 \text{ mm}^3$  (more than



15 mm length in the case of needles) have been grown in silica gels acetified with acetic acid.

2 Depending on the region of the gel, crystals of different morphologies have been obtained.

3 Dissolution of the early formed precipitates and dendrites followed by the recrystallization of the crystals has been observed (in the  $\text{CaCl}_2$  incorporated gels with  $\text{Na}_2\text{SO}_3$  as feed solution).

4 Incorporation of  $\text{Na}_2\text{SO}_3$  solution in gels resulted into spherulites whereas good quality single crystals have been obtained using  $\text{CaCl}_2$  incorporated gels.

5 In the U-tubes, in the gel nearer to  $\text{Na}_2\text{SO}_3$  feed solution, good quality single crystals have been obtained compared to those in gel near  $\text{CaCl}_2$  feed solution.

#### REFERENCES

- 1 Blank, Z., Brenner, W.: J. Cryst. Growth 11, 255 (1971).
- 2 Blank, Z.: J. Cryst. Growth 26, 215 (1974).
- 3 Patel, S.M., George, V.: J. Electronic Mater. 6, 499 (1977).
- 4 GarciaRuiz, J.M.: J. Cryst. Growth 75, 411 (1986).
- 5 Arend, H., Perison, J.: Mater. Res. Bull. 6, 1205 (1971).

- 6 Arend, H., Hubber, W.: J. Cryst. Growth 12, 179 (1972).
- 7 Konak, C., Smutny, F., Brezina, B., Budik, L.: Czech. J. Phys. B27, 1313 (1977).
- 8 Liaw, M., Faust, J.W.: J. Cryst. Growth 8, 8(1971).
- 9 Kratochvil, P., Sprusil, B.: J. Cryst. Growth 3/4, 360 (1968).
- 10 Joshi, M.S., Antony, A.V.: J. Mater. Sci. 2, 31 (1980).
- 11 Khatkhede, M.G.: M. Phil. Thesis (1990) Shivaji University (India).
- 12 Glocker, D.A., Soest, I.F.: J. Chem. Phys. 51, 3143 (1969).
- 13 Patel, A.R., Venkateswara Rao, A.: Bull. Mater. Sci., 4, 527 (1982).
- 14 Waerstad, K.R., Schib, R.M., McClellan, G.H.: J. Appl. Cryst. 7, 447 (1974).
- 15 Matsuno, T., Koishi, M.: J. Cryst. Growth 66, 135 (1984).
- 16 Matsuno, T., Koishi, M.: J. Cryst. Growth 71, 263 (1985).
- 17 Halberstadt, E.S., Henisch, H.K.: J. Crystal Growth 3/4, 363 (1968).
- 18 Burnham, C.E.: Geol. Soc. Amer. p. 29 (1967).
- 19 Matthews, F.W., McIntosh, A.D.: Canad. J. Res. 26B, 747 (1948).

- 20 Hanoka, J.I.: J. Appl. Phys. 40, 2694 (1969).
- 21 Bloor, D.: J. Cryst. Growth 7, 1 (1970).

Table-1: Power diffraction data for  $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$

$d_{\text{obs}}$	$d_{\text{cal}}$	hkl	I/I <sub>0</sub>
3.802	3.802	121	57.34
3.180	3.121	031	2.44
2.683	2.670	122	1.10
2.451	2.452	400	1.57
2.221	2.257	331	9.29
2.217	2.205	241	9.15
2.124	2.122	013	22.98
-	2.115	322	-
-	2.114	103	-
2.060	2.062	042	0.55
1.992	1.928	431	2.06
1.811	1.800	440	100.00
1.779	1.780	313	6.11
1.773	1.744	342	4.87
1.566	1.677	252	3.52
1.622	1.624	004	5.75
1.584	1.585	601	1.81
1.581	1.584	114	6.65
1.521	1.520	621	0.49
1.458	1.477	433	2.23
1.422	1.421	542	20.59
1.251	1.252	125	2.43