CHAPTER 5

GROWTH OF RHT SINGLE CRYSTALS IN SILICA HYDROGEL

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5.1 Introduction

The importance of the gel method and its performance to other crystal growth techniques were emphasized in Chapter 1. Quite a few number of materials are grown as single crystals all over the world in recent years, some with relative ease and other after long and careful modification of the method itself. Nevertheless, there are still many materials which are either not yet grown at all or not in the right form or atleast not with sufficient size, purity and perfection. In fact, research in the direction of upgrading the level of knowledge of the structure and properties of solids would benefit by the availability of more and more suitable crystalline materials. The aim of the present work is to place the gel technique on an anvil and thus to test it's performance and potentiality in producing transparent larger and more perfect single crystals. In the case of RHT, which will fail to be crystallized by all high temperature methods because it decompose (201^{o}C) before melting. The solution growth method is obviously not applicable on account of their poor solubility (1.18 gm/100 cc at 25°C) in water. This material therefore, offers an excellent example among others, to investigate and devise better and newer growth procedures to test for the wider usefulness and merit of the gel technique. A literature surveyed showed that no studies are carried out on the growth of RHT crystals. The present chapter describes the growth of RHT single crystals in silica hydrogel.

5.2 Preparation of Silica Gel

The solution of commercial sodium metasilicate was centrifused at 15,000 rpm for half an hour to separate out the floating and suspended impurities. As a result, transparent golden coloured solution of soidum metasilicate was obtained and can be preserved as a stock solution for quite a longer period. This solution was kept away from contact with atmosphere to avoid absorption of carbon dioxide[1]. To this pure sodium metasilicate solution, the required quantity of double distilled water was added to give a resulting solution of specific gravity 1.03 to 1.07 gm cm^{-3}, as and when it was required.

As described in Chapter 1, gel

formation takes place due to polymerization when it is mixed with any mineral or organic acid. The period required for gelation depends on density, pH of gel solution, different acid used, and temperature. Plank[2)] showed that the gelation time is very sensitive to pH, because of a gradual liberation of hydroxyl-ions. The gel is considered ready for use when it resists pouring. However, the gelling process is not completed at that time because the gel medium always evolves with time[3)]. When linked with a standard procedure, Hurd and Letteron[4)] and Alexander[5)] have described such procedures.

5.3 Experimental

All the growth experiments were conducted in glass test tubes of length 25 cms. and inner diameter 2.5 cms. The chemicals used for growing crystals were :

(i) Commercial sodium metasilicate (98 %).

(ii) B. D. H. AnalaR grade tartaric acid (99.5 %).

(iii) Fluka-Garantie rubidium chloride (98.0 %).

In order to grow RHT single crystals in the gel medium, the following chemical reaction was employed :

$$(CHOH.COOH)_2 + RbCl \longrightarrow RbHC_4H_4O_6 + HCl \quad (5.1)$$

Figure 5.1 shows a schematic diagram of the growth system. In the present work, rubidium chloride and tartaric acid solutions were prepared by dissolving them in a appropriate amount of double distilled water to give the required strength.

Gels were prepared by acidifying the solution of sodium metasilicate of required specific gravitity by adding calculated amount of double distilled water to the stock solution at the time of setting the experiments. Tartaric acid solution of different molarity was added drop by drop with a pipette to the above sodium metasilicate solution with constant stirring to avoid excessive local ion concentration which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbied.

The electrodes of pH meter (Systronics, Digital pH meter, Model 335) were immersed in meta-silicate solution, as pH plays very crucial role in the growth mechanism. It was found that changes in pH were not of very large in magnitudes with the addition of tartaric acid, as this acid is a weak organic acid. After getting desired value of pH, the solution was transferred to test tube without giving any chances for the formation of air bubbles, the formation of which will hinder the growth. Test tubes were closed with cork to prevent the evaporation and contamination of the surface.

The gel pH range 3 to 6 was usually found to set in 2 to 6 days, depending on the environmental temperature. After ensuring firm gel setting, the growth experiments were started by adding the feed solution of rubidium chloride of varying strength from 0.5 M to 2.0 M above the set gel with the help of a pipette, the drops from the pipette using allowed to fall along the walls of the test tubes in order to prevent the gel surface from breaking.

5.4 Results

For lower concentration (0.25 M) of

rubidium chloride solution, the nucleation started appearing after 4 to 5 days, whereas, for higher concentration above 1.5 M, the nucleation started within few hours. In all cases growth experiments were completed in 15 to 20 days. It was found that lower concentration gave rise to good quality transparent RHT crystals, whereas higher concentrations gave rise to hollow and dendritic RHT crystals. The decrease in the concentration of rubidium chloride solution increased the distance of nucleation sites from the gel interface. The experimental details and growth parameters are summarised in Table 5.1. The results are based on the statistical average of five sets of experimentas. Figure 5.2 illustrates the growth of RHT crystals in the gel medium and Figure 5.3 shows some typical crystals of RHT grown in the present work.

5.5 Discussion

According to equation (5.1), single crystals of RHT are obtained. The tubes in which the gel surface was a bit loose resulted in the growth of opaque RHT crystals, immediately below the gel solution

Table 5.1

Growth parameters for growing RHT single crystals

Concentration of incorporated tartaric acid solution (M)	Concentration of rubidium chloride solution (M)	Growth period (days)	Size of grown crystals (mm^3)	Quality of the grown crystals
1	2	3	4	5
0.5	0.5	20	2 x 1 x 1	p
	1.0	15	4 x 2 x 2	p
	1.5	15	5 x 2 x 2	m
	2.0	15	7 x 2 x 2	g
1.0	0.5	12	6 x 3 x 2	p
	1.0	9	11 x 4 x 3	g
	1.5	9	16 x 5 x 3	v.g.
	2.0	9	8 x 3 x 2	m

Table 5.1 (contd.)

1	2	3	4	5
1.5	0.5	10	6 x 4 x 2	g
	1.0	10	7 x 4 x 2	m
	1.5	10	12 x 4 x 3	v.g.
	2.0	10	9 x 5 x 2	p
2.0	0.5	12	14 x 3 x 2	g
	1.0	12	10 x 2 x 2	m
	1.5	12	12 x 4 x 2	p
	2.0	12	8 x 3 x 2	p

p - poor m - medium g - good v.g. - very good interface. Properly set tubes, on the other hand, resulted in excessive nucleation, both transparent and opaque RHT crystals are seen growing side by side in a single test tube. The opaque crystals are observed to grow faster than the transparent ones. This may be because when a cyrstal grows, it bodily displaces the polymer and consequently, the neighbouring pores which facilitate diffusion are pressed and narrowed. This continuous for quite sometime until the pores become so fine that the diffusion of nutrients towards the crystal is eventually retarded, thereby decreasing the reaction velocity to generate a transparent RHT crystal. But on the other hand, if the growing matrix incorporates the gel particles, causing the least deformation of the neighbouring gel volume when result is an opaque RHT crystals. A few RHT crystals, which nucleated and grow towards the bottom of the tube, are found to have suffered anion defeciency and hence their growth is very slow.

The occurrence of various habits of crystals in different regions of the growth medium canbe attributed to different concentration gradients and growth rates. In the present investigation, dendritic and hollow crystals of RHT are found to grow in the regions of high concentration gradients when growth rate is high. Perfection of a crystal is influenced by the rate of arrival of solute at the crystal surface. Growth of more perfect crystals should be expected through slow diffusion. Away from the gel interface, rate of diffusion of the feed solution gradually slows down in the gel, and when it becomes steady, well developed needle shaped, rod-like and platy transparent RHT crystals result. The details of habit and morphology are dealt in Chapter 7.

5.6 Conclusions

1. Gel technique can successfully be employed for the growth of single crystals of RHT.

2. Colourless transparent and bright RHT single crystals up to 16 x 5 x 3 mm^3 in size are obtained.

3. By changing the concentration of feed solutions, RHT crystals with different

morphology are obtained.

4. Restricted amount of gel inclusion takes place in the platy crystals.

5. The waste product of reaction affect the size and transparency of the growing RHT crystals.

REFERENCES

1. R. M. Patel : Ph. D. Thesis M. S. University of Baroda, Baroda (1980).

2. A. C. Plank : J. Colloid Sci. 2 (1947) 413.

3. H. K. Henisch : "Crystal Growth in Gels", (Pennsylvania University Press, University Park, PA (197).

4. C. B. Hurd and H. A. Letteron : J. Phys. Chem. 36 (1932) 604.

5. G. B. Alexander : J. Am. Chem. Soc. 75 (1953) 5655.

Captions of the figures

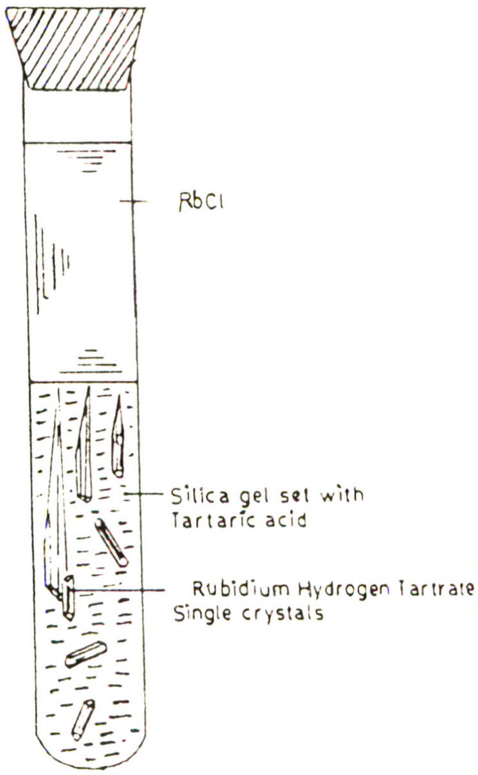

Fig. 5.1

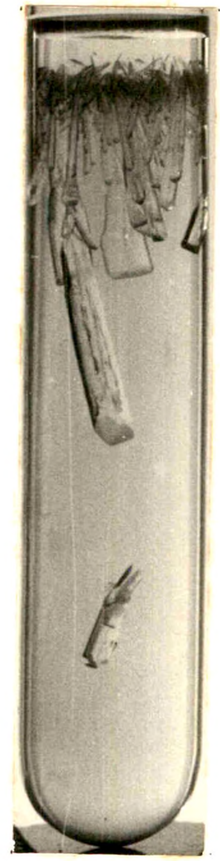

Fig. 5.2

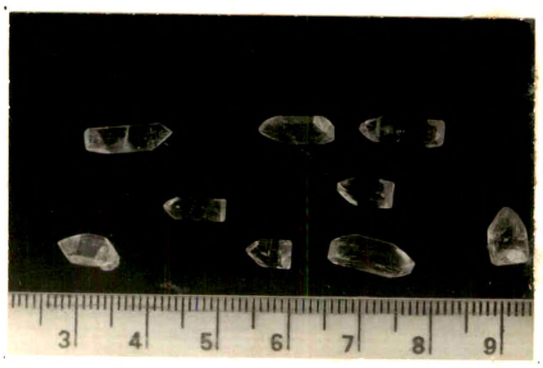

Fig. 5.3