Bull. Mater. Sci., Vol. 27, No. 4, August 2004, pp. 323–325. © Indian Academy of Sciences.

Growth features of ammonium hydrogen *d*-tartrate single crystals

G SAJEEVKUMAR*, R RAVEENDRAN, B S REMADEVI† and ALEXANDER VARGHESE VAIDYAN#

Department of Physics, S.N. College, Kollam 691 001, India
†Department of Physics, S.N.W.C., Kollam 691 001, India
#Department of Chemistry, St. Stephan's College, Pathanapuram 689 695, India

MS received 20 March 2004; revised 9 June 2004

Abstract. **Ammonium hydrogen *d*-tartrate (*d*-AHT) single crystals were grown in silica gel. The growth features of these crystals with variation of parameters like specific gravity of the gel, gel pH, acid concentrations, concentration of the feed solution and gel age were studied in detail.**

Keywords. ***d*-AHT single crystals; growth features.**

1. Introduction

Most of the tartrate compounds are insoluble in water and decompose before melting. Hence, single crystals of such type cannot be grown either by slow evaporation or by melt technique, but can be grown easily by gel method. Gel method is an alternative method to solution growth with controlled diffusion and the growth process is free from convection. Henisch (1970, 1973) has done an extensive survey of the gel technique.

Among the various crystal growing methods, the gel method is found to be the best one for growing single crystals of *d*-AHT. Many crystal growers (Patel and Rao 1978; Kurian and Ittyachen 1980; Suib 1980; Desai and Hanchinal 1983; Desai and Rai 1987; Annie Kuruvila 1992) have grown *d*-AHT crystal by the gel method, but in the literature survey there is no systematic study of the growth features of these crystals with variation of parameters like the specific gravity of the gel, gel pH, concentration of the tartaric acid, concentration of the feed solution, gel age etc are found. Thus we intend to make a systematic study of the variations in the growth features of these crystals.

2. Experimental

Silica gel was prepared by mixing sodium metasilicate solution (specific gravity, 1·04 g/cc) with *d*-tartaric acid solution having different molar concentrations in different amounts. Crystallization was carried out in standard test tubes of dimensions 2·5 mm diameter and 20 mm length. The gel was usually set within 4 to 18 days, depending on the gel density, pH of the gel solution and ambient temperature. After ensuring proper gel setting, the growth process was started by adding ammonium bromide as the feed solution above the set gel with the help of a pipette. Several ammonium salts can be used as the feed solution. A comparative study of the effect of ammonium iodide, ammonium chloride and ammonium acetate as feed solution was carried out. In all the cases, the growth and morphology remained more or less the same. Ammonium bromide was the best-feed solution among the ammonium halides. This was due to the fact that bromine being lower down the reaction series, the hydrobromic acid, which was evolved as a waste product, was less reactive than the hydrogen chloride, which was released while using ammonium chloride as the feed solution. Ammonium iodide would have been better, but the iodide gets oxidized. The feed solution diffused into the gel slowly and reacted with the gel-incorporated tartaric acid forming transparent, geometrically well-defined single crystals of ammonium hydrogen *d*-tartrate in the test tube.

There are basically three regions in a test tube where the crystal nuclei have opportunities to grow. They are: (i) the interface between the gel and the feed solution, where reaction between feed solution and gel takes place resulting in the production of crystal nuclei. The interface is also the site where syneresis takes place, (ii) the central part of the test tube. The feed solution percolates through the pores of the gel and reacts with the gel acid. The crystal nuclei begin to develop in the gel pores of the central part of the tube and (iii) the walls and the bottom of the test tube. The feed solution can also slip through some space between gel and tube walls. The solution reacts with the impregnated acid in the gel, with the formation of crystal nuclei near the wall and bottom of the test tube.

The crystals were collected separately from all these regions after allowing sufficient time for nucleation and subsequent growth (6 to 8 weeks).

*Author for correspondence

3. Results and discussion

A large range of concentrations of reactants (tartaric acid impregnated gel and ammonium bromide) was used to determine optimum conditions for the growth of good quality single crystals of *d*-AHT. From the experiments it was found that the minimum concentration of the tartaric acid for initiating the growth of crystals was 0·5 M. Below this concentration gelation was impossible. For any molar concentration of tartaric acid in gel, 10% TA in 90% SMS forms precipitates and not the gel. With 20% TA in 80% SMS, gelation takes place, the gel becomes translucent. With 30% TA, the gel becomes transparent. The pH value does not play a significant role in the formation of the gel. Further, it does not affect the morphology of the growing crystal. However, it is the quantity of acid in gel, which determines the habit of the crystal. It is, therefore, possible to grow crystals by varying the concentration of the tartaric acid from 0·5–5·099 M, which corresponds to the saturated solution of tartaric acid in water at room temperature. For lower concentration (between 0·5 M and 1·5 M) the quantity of tartaric acid should be more than 50% to obtain crystals of good geometrical shape.

The concentration of the feed solution was varied from 1·5–3·5 M. For concentration < 1·5 M, the ability of the feed solution to diffuse was greatly diminished, thereby decreasing the probability of formation of crystal nuclei and subsequent growth. For feed solution concentration > 3·5 M, where the tartaric acid concentration in gel is < 3·5 M, diffusion is heavy resulting in the growth of translucent crystals. But if the tartaric acid concentration is also 3·5 or more, good transparent crystals are obtained.

There were basically three habits of the *d*-AHT crystals grown in silica gel. They were: (i) needle shaped crystals (figure 1), (ii) orthorhombic disphenoidal crystals (figure 2) and (iii) sphenoidal (tetrahedral) crystals (figure 3).

The needle shaped crystals generally indicate the shape similar to that of a needle. In the present case, the name indicates an accelerated growth along one direction as compared to the growth along different directions, thereby thickening the needle and giving rise to many faces (more than eight faces). The needle starts growing from a bunch of nuclei at the interface between the gel and the feed solution. With the timely arrival of feed solution they start getting separated as fine needles. The gradual deposition of crystal material thickens the needle and also extends its growth along one direction viz. c-axis, which is the growth direction of *d*-AHT crystals of different habits. Further, it does not coincide with the vertical axis of the test tube.

The orthorhombic disphenoidal and sphenoidal crystals were normally found in the central part and bottom part

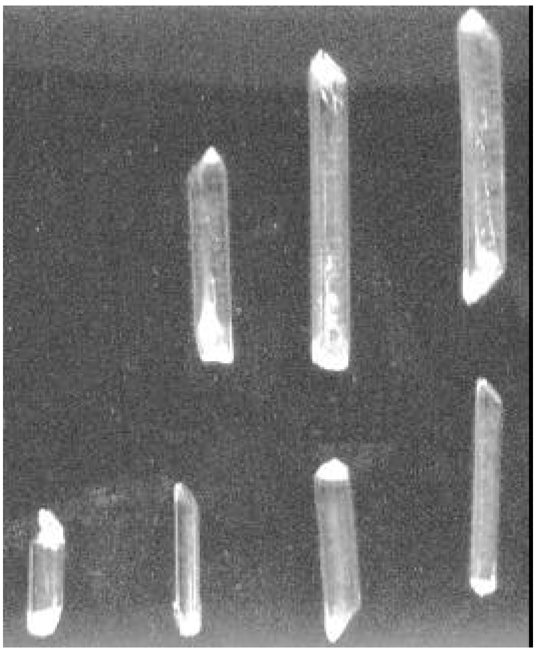

Figure 1. Needle shaped crystal ($22 \times 2 \times 2$ mm^3).

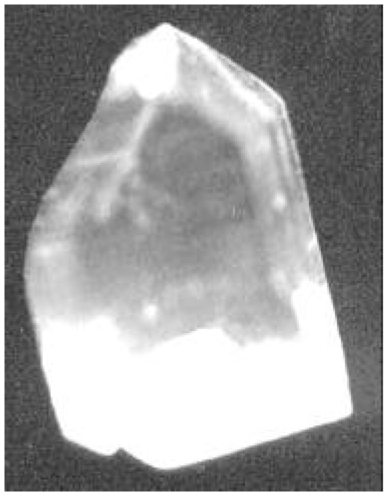

Figure 2. Orthorhombic disphenoidal crystal ($10 \times 8 \times 6$ mm^3).

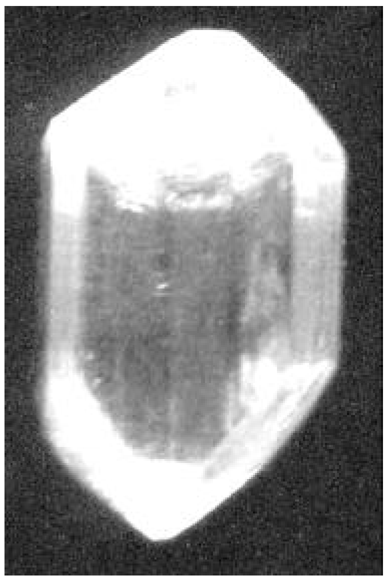

Figure 3. Sphenoidal crystal ($20 \times 10 \times 5$ mm^3).

Table 1. Gel pH and the linear growth of crystals.

TA conc.	% Acid with SMS	Gel (pH)	Gel setting time (days)	Crystal morphology maximum linear growth (mm)		
				Needle	Orthorhombic disphenoidal	Spenoidal
2·5 M	20	2·60	4	31		
	30	2·45	7		18	10
	40	2·27	10		28	8
	50	2·07	14		25	18
	60	1·90	18			28
3·0 M	20	2·52	3	60		
	30	2·39	7		24	12
	40	2·20	11		30	10
	50	1·97	15		28	8
	60	1·80	18			14
3·5 M	20	2·45	4	40		
	30	2·30	7		18	9
	40	2·10	11		22	6
	50	1·85	14		28	8
	60	1·72	17			18

Table 2. Gel pH and the number of crystals in the tube.

% of tartaric with SMS	Gel (pH)	Gel setting time (days)	Conc. of FS (M)	Crystals in the tube
20	2·6	4	1·5	7
			2·0	12
			2·5	15
			3·0	23
			3·5	28
30	2·45	7	1·5	9
			2·0	11
			2·5	14
			3·0	12
			3·5	19
40	2·27	10	1·5	10
			2·0	14
			2·5	8
			3·0	22
			3·5	25
50	2·07	14	1·5	8
			2·0	11
			2·5	19
			3·0	10
			3·5	18
60	1·9	18	1·5	6
			2·0	10
			2·5	8
			3·0	12
			3·5	14

of the tube. The size and face of a grown crystal depends upon the amount of feed solution available to growing crystals. This can be qualitatively connected with various parts of the test tube in which crystals of different habits are grown.

Thus when a fairly large amount of feed solution was available, needle shaped crystals grow. With decreasing amount of feed solution, the habit becomes orthorhombic disphenoidal. With a further drop in the availability of feed solution, only sphenoidal crystals could be obtained. This also suggests rather an elegant method to grow crystals of the desired habit. In most of the grown crystals, c-axis happens to be the growth axis, which is inclined to the vertical. However, there are a few exceptions to these general observations. The habit and quality of the grown crystals depend not only on the amount of feed solution available at the site but also on the rate at which the material reaches that site. The deposit of molecules at appropriate places on a growing surface of a crystal is necessary for ordered growth. Further, some time is required for the molecules to settle at these places. If the rate of arrival of material on the growing surface is not commensurate with the above requirements, the crystals will be obviously of inferior quality. The observations were extended over a period of two months and tables 1 and 2 summarize the results of the experiments carried out. The tables indicate that with a suitable combination of conditions regarding concentration (pH), gel setting time etc, it is possible to grow crystals of desired morphology and size.

4. Conclusions

The study of various gel parameters on nucleation and growth of *d*-AHT crystals have clearly shown that:

(I) Quantity of acid has a dominating effect on the morphology of *d*-AHT crystals whereas gel pH and acid pH do not show any significant effect.

(II) For a wet and fungus free gel, the gel age does not noticeably affect crystal growth.

(III) Crystal habit is independent of the feed solution concentration. However, for the penetration and growth of crystals, the minimum concentration of feed solution should be 1·5 M.

(IV) Irrespective of the concentration of tartaric acid, the gel setting time for a particular quantity of acid is fixed.

(V) Needle shaped crystals are obtained at 20% of acid in gel irrespective of the molar concentration of the acid and feed solution.

(VI) Orthorhombic disphenoidal crystals are obtained for 30% and 40% of acid in gel.

(VII) Disphenoidal crystals are obtained for 50% and 60% of acid in gel.

References

Annie Kuruvila 1992 *Optical and related study of crystals* (*ammonium hydrogen d-tartrate single crystals*), PhD Thesis, M.S. University, Vadodara

Desai C C and Hanchinal A N 1983 *Bull. Mater. Sci.* **12** 1499

Desai C C and Rai J A 1987 *Surf. Technol.* **15** 131

Henisch H K 1970, 1973 *Crystal growth in gels* (University Park: The Pennsylvania University Press)

Kurian K V and Ittyachen M A 1980 *J. Mater. Sci.* **15** 1724

Patel A R and Rao A V 1978 *J. Cryst. Growth* **43** 351

Suib S L 1980 *J. Cryst. Growth* **48** 155