

On the growth of calcium tartrate tetrahydrate single crystals

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Abstract. Calcium tartrate single crystals were grown using silica gel as the growth medium. Calcium formate mixed with formic acid was taken as the supernatant solution. It was observed that the nucleation density was reduced and the size of the crystals was improved to a large extent compared to the conventional way of growing calcium tartrate crystals with calcium chloride. The role played by formate–formic acid on the growth of crystals is discussed. The grown crystals were characterized by atomic absorption spectroscopy (AAS), X-ray diffraction analysis (XRD), microhardness measurement, Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG) and differential thermal analysis (DTA). The results obtained are compared with the previous work.

Keywords. Gel growth; calcium tartrate; FTIR; thermal studies; microhardness.

1. Introduction

Tartrate crystals are of considerable interest, particularly for basic studies of some of their interesting physical properties (Yadava and Padmanabhan 1973; Desai and Patel 1987; Gon 1990; Abdel-Kader *et al* 1991). Calcium tartrate tetrahydrate crystals are found to be orthorhombic with lattice parameters: $a = 9.24 \pm 0.02 \text{ \AA}$, $b = 10.63 \pm 0.02 \text{ \AA}$, $c = 9.66 \pm 0.02 \text{ \AA}$ and the space group, $P2_12_12_1$ (Ambady 1968). For the growth of calcium tartrate crystals it is customary to diffuse calcium chloride solution into the gel charged with tartaric acid. It has been reported that (Sivanesan *et al* 1992; Henisch 1996) the size of calcium tartrate crystals growing in the gel did not improve even after applying nucleation control techniques like concentration programming and neutral gel methods.

Most of the earlier works (Henisch *et al* 1965; Armington *et al* 1967; Dennis and Henisch 1967) on pure calcium tartrate crystals were done with an aim of understanding the basic principles and the nature of crystal growth phenomenon, especially those involved in the gel technique. With an aim of controlling nucleation and improving the size, in the present study, we have grown pure calcium tartrate tetrahydrate single crystals using calcium formate mixed with formic acid as the supernatant solution. The grown crystals have been characterized by density measurement, AAS, XRD, microhardness measurement, FTIR, TG and DTA studies. The crystal growth and the role played by formate–formic acid are discussed.

2. Experimental

2.1 Crystal growth

The test tube diffusion method (Henisch 1996) was employed to grow calcium tartrate single crystals in a gel medium. 0.5 M sodium meta silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) was titrated with 0.5 M tartaric acid till the mixture attained the pH of 4.2. This gelling mixture was allowed to set in glass tubes of length, 200 mm and diameter, 25 mm. The gel was set in about 48 h. After a gel aging of one day, the supernatant solution was added over the set gel. The supernatant solution was a mixture of 0.5 M calcium formate and 85% formic acid so that the pH of the solution was between 1 and 1.5. The expected chemical reaction was



Small crystals appeared down the gel solution interface in about 2 days and large crystals with good morphological perfection appeared down the gel column within a week. The crystals were harvested after a month. The maximum size of the crystals grown was about $8 \times 6 \times 3 \text{ mm}^3$. A photograph of the crystals growing inside the test tube is shown in figure 1.

2.2 Density and microhardness

The density of the crystal was found using flotation method. The hardness of the crystals was obtained using Leitz Weitzier hardness tester at room temperature. The static indentation was done on the crystals by applying load varying from 5 to 50 g over a fixed interval of 10 s and

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removed. For each load (P), five impressions were made and the average of diagonal lengths (d) of the indentation mark was obtained.

The Vicker's hardness number (H_v) was calculated using the formula

$$H_v = 1.8544 P/d^2, \quad (2)$$

where P is in kg, d is in mm and H_v is in kg/mm².

2.3 AAS and XRD studies

The AAS studies were carried out using Perkin Elmer spectrophotometer. The atomic concentrations of Na, Si and Fe were determined in order to check the degree of purity of the grown crystals. The powder X-ray diffraction data were collected using JEOL-JDX 8030 X-ray diffractometer system available at the Central Electrochemical Research Institute, Karaikudi. The XRD pattern was used to identify the material and to determine the lattice parameters of the grown crystal.

2.4 FTIR and thermal studies

The FTIR spectrum of the grown crystals was recorded in the wavenumber range 400–4000 cm⁻¹ using Centaurps



Figure 1. Growth of calcium tartrate single crystals in the test tube.

FTIR spectrometer. The thermogram of the crystal was obtained with the help of Seiko 320 thermal analyser. Thermogravimetric analysis was carried out from room temperature to 900°C at a heating rate of 10°C in the atmosphere of helium gas.

3. Results and discussion

3.1 Crystal growth

It has been reported that (Halberstadt and Henisch 1968) calcium tartrate does not nucleate at pH values < 3. Also, during the growth of calcium tartrate crystals, the original tartaric acid content of the gel is completely exhausted partly through the formation of calcium tartrate crystals and partly through the demonstrable loss of tartaric acid to the solution at the top in the gel region close to the supernatant liquid. Normally, many small crystals grow in the gel medium and only a few of them are larger in size.

In order to suppress the nucleation and to improve the size of calcium tartrate crystals it is essential to eliminate the factors said above. We have tried to eliminate the first factor by using a suitable pH buffer and the second factor by acidifying the supernatant solution. Earlier works (Cipano *et al* 1990) have shown that the variation of the acidity of the crystallogenetic media strongly influenced the depth of the first crystal arising in the gel. They have used calcium chloride mixed with hydrochloric acid as the supernatant solution. The nucleation suppression is achieved by converting the tartrate ions ($C_4H_4O_6^{2-}$) present near the gel solution interface into its molecular form ($H_2C_4H_4O_6$) by proton introduction.

It was observed that the nucleation suppression near the gel solution interface was high when a strong acid, like HCl, was used. On the other hand, when a weak acid like formic acid was used, we observed that nucleation suppression was very high. The first crystal arising in the gel when HCl was used was about one inch deep into the gel, whereas it was 2–3 mm when formic acid was used. However, considering the size and perfection of the grown crystals we found that those crystals grown by using formate–formic acid as the supernatant solution were superior to those crystals grown with calcium chloride–HCl. Most of the crystals were larger in size and few crystals very close to the gel solution interface were smaller in size. The average length of the grown crystals was found to be 5.2 mm.

The growth veils reported by earlier workers (Armington *et al* 1967; Henisch 1996) are absent in the crystals grown by using formate–formic acid as the supernatant solution (figure 2 illustrates the absence of veils). It is expected that formate/formic acid acts as a pH buffer and maintains the pH of the gel medium throughout the growth process. Hence, the crystals growing deep into the gel are larger in size. In addition, formic acid prevents algae growth

which disturbs the growth of calcium tartrate crystals during long growth periods.

3.2 Density and mean mass of the grown crystal

The density of the crystal was found to be 1.817 g/cc. This value agrees well with the reported values of 1.836 and 1.818 g/cc (Armington *et al* 1967; Jesu Rethinam 1993). The mean mass of the grown crystals was found to be 92.8 mg when the pH of the supernatant solution was 1.0 and 81.3 mg when pH was 1.3. For the crystals grown from calcium chloride mixed with HCl, it was reported that (Cipano *et al* 1990) the mean mass was 39.4 and 46.5 mg for pH = 1.08 and 1.3, respectively.

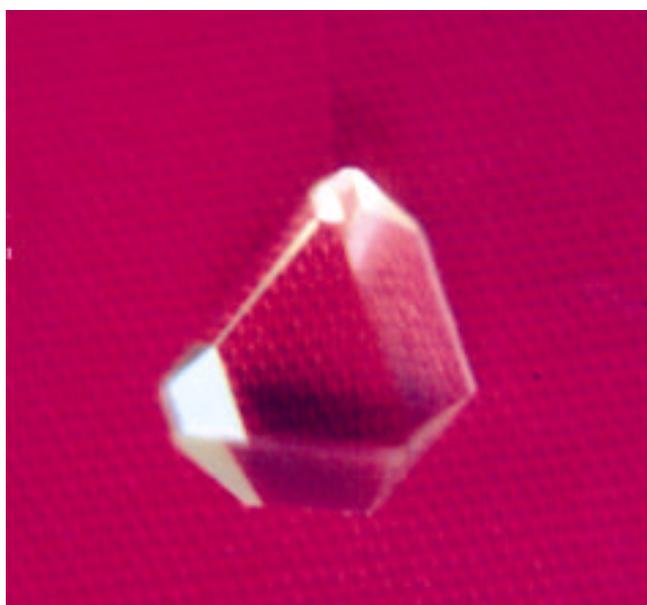


Figure 2. Photograph showing the absence of growth veils in the grown crystals.

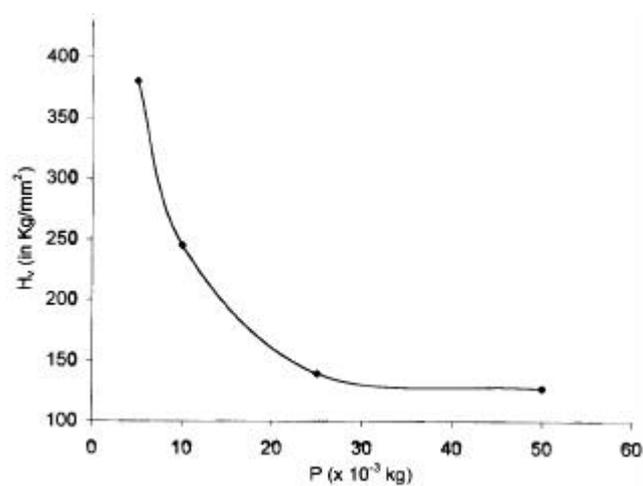


Figure 3. Variation of microhardness (H_v) with load (P).

3.3 Microhardness

The values of H_v were calculated using (2) for various loads and are plotted as shown in figure 3. It was observed that the microhardness was found to decrease initially with increasing load and became constant at higher loads. During indentation, the indenter first penetrates the distorted zone of the surface layer. Therefore, we observe a decrease in the hardness of the material for increasing load. As the depth of indentation increases with load, the effect of the inner layers become more and more prominent than the surface layers and the indenter reaches a depth at which undistorted materials exist and therefore, no change is observed in the value of hardness with load.

The hardness obtained for the crystals grown in the present study using Leitz Weitzier hardness tester at room temperature for a 50 g load was 127 kg/mm². The hardness of calcium tartrate crystals available in the literature (Armington *et al* 1967) using Leitz Durimet microhardness tester with a knoop indenter for a 100 g load was 111.2 kg/mm².

We have determined the work hardening coefficient, n , from the slope of $\log P$ vs $\log d$ plot (not shown) using least square fit method. The value of n was found to be < 2 . According to theory (Onitsch 1947), if $n < 2$, the materials are said to be hard ones. He also found that microhardness decreases with increasing load when $n < 2$ and increases with load when $n > 2$. The decrease in H_v for increasing load, P , observed in the present study is in good agreement with the theoretical prediction and calcium tartrate crystals grown in the present study fall in the category of hard materials.

3.4 AAS and XRD studies

The atomic concentrations obtained by AAS in the grown crystals were 1.167, 11.834 and 2 ppm for Fe, Na and Si, respectively. Trace atomic concentrations of Na and Si show that the grown crystal was not contaminated by the gel. The atomic concentration of Fe was determined be-

Table 1. Indexed XRD data for calcium tartrate tetrahydrate crystals.

hkl	From present work		From JCPDS file	
	$2q$ (°)	I/I_0	$2q$ (°)	I/I_0
101	13.4	100	13.283	100
020	16.9	66	16.777	35
200	18.5	58	18.430	35
121	21.5	44	21.446	20
122	27.2	35	27.275	10
301	29.5	43	29.454	40
321	34.0	29	34.088	18
041	35.5	69	35.336	55
232	37.0	23	37.104	4
223	38.7	23	38.696	8

cause the starting materials used in the present work had a slightly higher ppm level of Fe compared to other elements in it.

XRD has confirmed the material of the grown crystals. The indexed XRD data for the grown crystals are given in table 1. The diffraction data match very well with the JCPDS data for calcium tartrate tetrahydrate crystals. The lattice parameters obtained in the present study are: $a = 9.227(13)$, $b = 10.622(28)$, $c = 9.652(8)$ Å which compares very well with the reported lattice parameters (Ambady 1968).

3.5 FTIR and thermal studies

The FTIR spectrum of the grown crystals recorded in the wavenumber range 400–4000 cm^{-1} is shown in figure 4. The two strong peaks at 3565 and 3425 cm^{-1} are due to OH stretching mode and to water. The band at 1588 cm^{-1} is attributed to the C=O stretch of carbonyl group. The strong peak at 1385 cm^{-1} is assigned to C=O symmetric and $d(\text{O}-\text{C}=\text{O})$ mode. The peak at 1148 is due to C–H vibrational modes. The peaks of various intensities at 1061 and 1011 cm^{-1} are due to out of plane O–H deformation and C–O stretching. The absorption between 964 cm^{-1} and 534 cm^{-1} is due to calcium–oxygen. The FTIR spectrum obtained in the present study is similar to the IR spectrum of calcium tartrate crystals reported earlier (Selvarajan *et al* 1993; Vimal and Mihir 2001). The observed vibrational frequencies and their assignments are listed in table 2. FTIR spectrum revealed the presence of water molecules, O–H bond, C–O and carbonyl C=O bonds.

The mechanical stiffness constant was calculated for C=O vibration at 1588 cm^{-1} using the relation,

$$n = 1303 \{F(1/m_1 + 1/m_2)\}^{1/2}, \quad (3)$$

where $m_1 = 16$ a.m.u., $m_2 = 12$ a.m.u., F the force constant and n the stretching vibration. The value was found to be 1018 Nm^{-1} which agrees very well with the reported value, 1020 Nm^{-1} (Vimal and Mihir 2001).

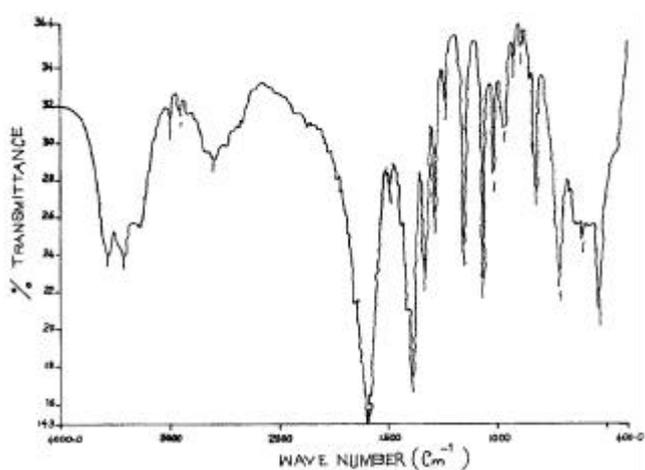


Figure 4. FTIR spectrum of calcium tartrate single crystals.

The TG, DTG and DTA thermograms of the grown crystals are shown in figure 5. It is noticed that the sample loses water of hydration and becomes anhydrous at 192°C and thereafter it decomposes into calcium oxalate and further decomposes into calcium carbonate at 667°C and finally turns into calcium oxide at 807°C and remains stable up to the end of the analysis. It was estimated that four water molecules were associated with the crystals. In the DTA curve we observe two endothermic peaks at 164 and 290.2°C and an exothermic peak at 438.8°C.

Thermal studies showed that these crystals are thermally unstable beyond 112°C and there is no physical transformation independent of mass change or decomposition of calcium tartrate crystals. Thermal studies on calcium tartrate tetrahydrate crystals reported earlier (Selvarajan *et al* 1993) grown from calcium chloride showed that the crystals started decomposing at 85°C and finally decomposed into calcium oxide at 420°C. However, in the present study we observed that the decomposition started at 112°C and decomposed finally into calcium oxide at 807°C. This shows that the crystals grown in the present study are thermally more stable than the reported one.

Table 2. FTIR spectral data for calcium tartrate crystals.

Band (cm^{-1})	Assignment
3565	OH stretching
3425	OH stretch (water)
2987	CH stretch
1588	C=O stretch
1385	$g(\text{C}=\text{O}) + d(\text{O}-\text{C}=\text{O})$
1330	OH plane bending
1148	$d(\text{C}-\text{H}) + p(\text{C}-\text{H})$
1061	O–H deformation
1011	C–O stretching
964–534	Ca–O mode

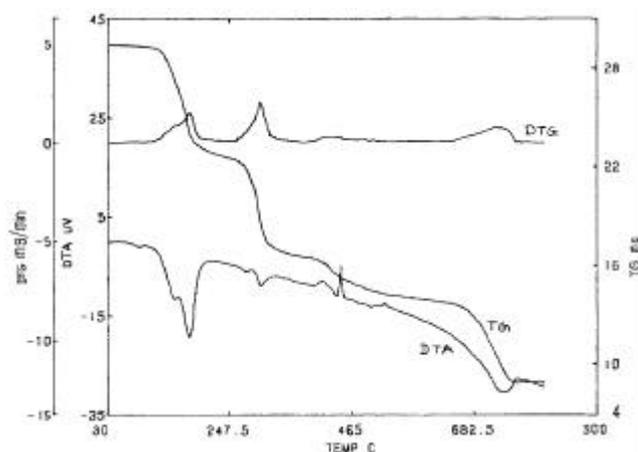


Figure 5. TG, DTG and DTA curves of calcium tartrate single crystals.

4. Conclusions

Calcium tartrate crystals were grown in silica gel with calcium formate mixed with formic acid as supernatant solution. Nucleation was reduced and size of the crystals growing deep into the gel was improved a lot compared to the crystals grown with calcium chloride as supernatant solution. It is concluded that calcium tartrate crystals grown from formate–formic acid are better than the calcium tartrate crystals grown by other methods reported so far.

From microhardness measurements we conclude that the grown crystals belong to hard materials. XRD confirmed the material of the grown crystal to be calcium tartrate tetrahydrate. AAS studies confirmed that the crystals grown by this method was not contaminated by the gel.

The FTIR spectrum of the grown crystals revealed the presence of O–H, C–O and C=O bonds. The presence of water molecules were detected. From the thermogram it is concluded that calcium tartrate crystals are thermally unstable beyond 112°C and decomposes into calcium oxide through many stages.

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