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Growth characterization and etching studies of calcium tartrate single crystal grown using tamarind extract

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Calcium tartrate crystals were grown in silica gel by single diffusion method. The reactants used were calcium chloride and extract from tamarind juice. Crude as well as centrifuged tamarind extracts were used. The studies on the growth parameter of the crystal were conducted. The characterization studies such as XRD, FT-IR, TG-DTA of the grown crystals were done and it was then compared with that of calcium tartrate crystals grown using AR grade tartaric acid. The absorption spectral, CHN analysis and etching were also studied.

Keywords: Gel growth, Calcium tartrate, XRD, FTIR, Thermal studies, Etching studies

1 Introduction

Good crystals can occasionally be grown in substances that are normally classified as gels. It has been observed that gels, in particular silica gel, are the best and most versatile growth media. Crystal growth using gel method is useful for substances having low solubilities and low dissociation temperature. The gel method is applicable to study the biological crystals. In the present work, the crystals were grown using tamarind juice and calcium chloride. The grown crystals were characterized by X-ray diffraction (XRD), Fourier Transform infrared (FTIR) spectroscopic techniques, Thermo Gravimetric (TG) and Differential Thermal (DT) analysis, CHN analysis, Atomic Absorption Spectral (AAS) and Etching studies.

2 Experimental Details

Calcium tartrate crystals were grown using gel method. Single diffusion method was adopted. The reactants used are tartaric acid impregnated silica gel and calcium chloride. Tartaric acid was extracted from tamarind. The extraction of tartaric from natural tamarind is time consuming and great care must be needed for its preparation. Crystals were grown both from centrifuged as well as crude tamarind juice.

The density of the gel plays an important role in the growth of the crystals. Here, gel of density 1.05 was used since this gives the best results. Below 1.05, the medium is soft. and above 1.06, the gel becomes more denser and shows concoidal fracture surface similar to glass. The pH has an important role in the growth of the crystal. The calcium tartarate tetrahydrate crystals of maximum size: 5 mm × 4 mm × 2 mm can be harvested, when the pH of the gel is 7. The effect of pH on the growth of these crystals is shown in Figure 1. When the pH of the gel varies, the morphology of the crystal also varies. In the case of calcium tartarate crystals, when the pH of the gel was below 6.5 no crystal was grown and when it was above 7.5, the number of crystals formed are very less.

The ageing of the gel has a profound effect on the quality and morphology of the crystals. The pore size distribution of the gel was affected by ageing. Hence, the gel having proper age produces good quality crystals with proper size. When 1 M calcium chloride

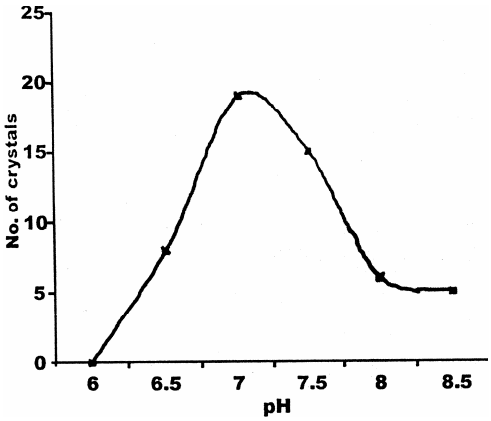


Fig .1—pH versus number of crystals

solution is used, very large number of tiny crystals were formed. The crystals were transparent, but they were very small in size. When 0.5 M solution is used, the crystals were good in size.

It was found that gel of pH between 6.5 and 7.5 gives the best results. In order to obtain good quality well faceted crystals, the concentration of supernatant solution (calcium chloride) should be maintained at 0.5 M. The density of sodium metasilicate should be 1.05 g/cc and the time needed to set the gel properly was found to be one to two days. Immediately after the addition of supernatant solution, a white precipitate was formed over the set gel and after one or two days well faceted crystals begin to grow within the gel. The grown crystals were harvested within a month. The number of crystals were greater near the interface, but the size of the crystals were small. As we go deep into the gel, the number of crystals formed will be less, but the size of the crystal will be large. The gels of insufficient density take longer time to set and are mechanically unstable. Very dense gel produces poor crystals because greater gel density causes poor pore size and hence, decrease the diffusion rate. This in effect leads to reduction in nucleation density. It was also observed that when tartaric acid extracted from tamarind is kept for days its colour changes to brown. The crystals grown out of fresh crude juice are transparent, compared to that grown out of aged centrifuged tamarind juice. The morphology of the well faceted good quality crystal is shown in Fig. 2.

3 Characterization and Etching Studies

3.1 X-ray diffraction studies of grown calcium tartrate crystals

The X-ray diffraction of the grown calcium tartrate crystals was studied using X-ray diffractometer (Burker AXSD 5005) at room temperature by using CuK_α radiation for a range of Bragg angle 2θ ($10^o < 2\theta < 60^o$) at the scanning rate of 0.05^o/s.

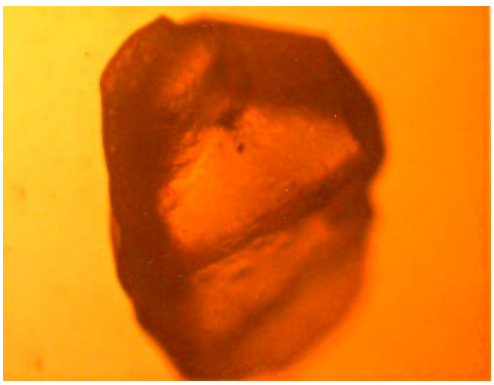


Fig. 2—Grown crystal of calcium tartrate (magnification × 400)

The calcium tartrate crystals prepared from crude tamarind juice as well as centrifuged tamarind juice were subjected to XRD studies. The results were then compared with the XRD studies of calcium tartrate crystals prepared from AR grade tartaric acid[1] . XRD data of calcium tartrate crystals prepared from centrifuged tamarind juice is found to be similar to that of the crystal grown using AR grade tartaric acid. XRD data of crystals grown out of crude tamarind juice does not match with that grown out of AR grade tartaric acid. This may be due to the presence of other compounds in crude tamarind juice which goes within the crystal matrices. On centrifuging, the major portion of these compounds are filtered.

The XRD patterns of the crystals grown from crude tamarind juice and centrifuged tamarind juice are shown in Figs 3 and 4, respectively. The corresponding XRD data are presented in Tables 1 and 2, respectively.

The XRD data of calcium tartrate crystals prepared from centrifuged tamarind matches with that of crystals prepared from AR grade tartaric acid (Table 3).

The crystal data of calcium tartrate crystals prepared using AR grade tartaric acid is presented in Table 4.

Table 1—XRD data of calcium tartrate crystals grown from crude tamarind juice

Angle 2-theta	*d* value (Å)	Intensity	Intensity count %
12.781	6.920	3.18	30.7
13.711	6.453	4.10	39.6
17.162	5.162	5.04	48.7
18.813	4.713	4.40	42.5
21.959	4.044	8.13	78.5
29.421	3.033	2.05	19.8
29.864	2.9894	3.17	30.6
32.315	2.7680	1.91	18.4
33.704	2.6570	2.19	21.1
35.547	2.5234	5.41	52.2
35.838	2.5036	8.34	80.6
37.039	2.4251	2.16	20.9
41.594	2.1695	3.34	32.3
41.885	2.1551	2.09	20.2
42.694	2.1161	1.45	14.0
48.288	1.8832	1.91	18.4
51.315	1.7790	2.36	22.7
51.926	1.7595	10.4	100.0
59.386	1.5550	2.26	21.8

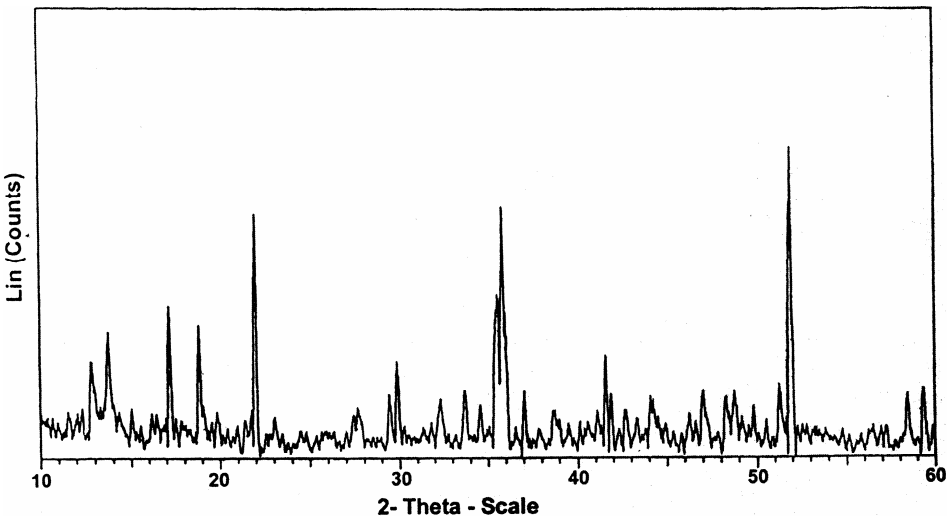


Fig. 3—XRD pattern of calcium tartrate crystals grown from crude tamarind juice

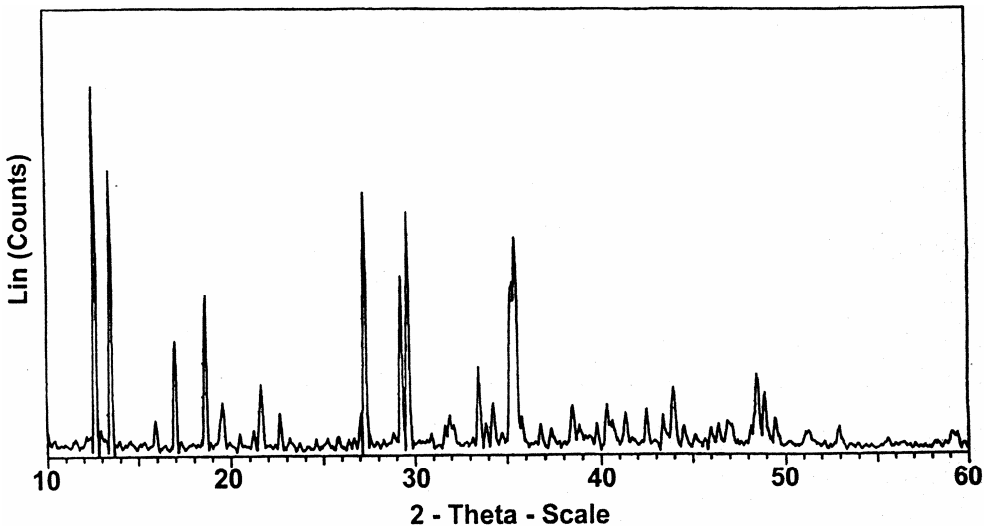


Fig. 4—XRD pattern of calcium tartrate crystals grown from centrifuged tamarind juice

The data observed from powder diffraction is well correlated with the data available in the literature[1,2]. Hence, the grown crystals have orthorhombic structure and the crystal structure is the same as that presented in Table 4. We have utilized the crystals grown from centrifuged tamarind juice for all the other studies which included in this paper

3.2 FTIR spectroscopic analysis of the grown calcium tartrate crystals

In the present investigation, KBr pellet method is used. The instrument used is Thermo Nicolet Avatar 370. The spectrum was recorded in the region 4000-500 cm^{-1} at room temperature. The infrared radiation promotes transitions in a molecule between rotational and vibrational energy levels of the ground electronic energy states. The FTIR spectrum of the grown calcium tartrate crystal is shown in Fig. 5.

The peaks observed at 3564.47 cm^{-1} and 3426.11 cm^{-1} are due to OH stretching mode and water[2]. 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 δ (O-C= 0) modes. The peak at 1148 cm^{-1} is due to C-H vibrational mode. The peaks at 1061 cm^{-1} 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

Table 2—XRD data of calcium tartrate crystals grown from centrifuged tamarind juice

Angle 2-theta	*d* value (Å)	Intensity	Intensity count %
12.602	7.019	53.7	100.0
13.453	6.576	41.6	77.5
15.881	5.576	4.95	9.2
16.955	5.225	16.5	30.7
18.597	4.767	22.9	42.7
19.523	4.543	7.53	14.0
21.595	4.112	10.1	18.8
22.623	3.927	5.91	11.0
27.277	3.267	38.3	71.4
29.244	3.051	25.7	47.9
29.623	3.013	35.3	65.9
33.482	2.6741	12.5	23.4
32.255	2.6155	7.35	13.7
35.246	2.5443	24.4	45.4
35.467	2.5289	31.4	58.5
38.489	2.3370	6.94	12.9
40.335	2.2342	7.13	13.3
41.364	2.1810	5.79	10.8
42.504	2.1251	6.42	12.0
43.980	2.0571	9.48	17.7
48.537	1.8741	11.3	21.0
48.938	1.8597	8.71	16.2

Table 3—Comparison of XRD data of calcium tartrate crystals

hkl	Calcium tartrate crystals prepared from centrifuged tamarind juice		Calcium tartrate crystals prepared from AR grade tartaric acid granules	
010	12.602	100	12.747	12.1
101	13.453	77.5	13.295	71.2
111	15.881	9.2	15.756	7.6
020	16.955	30.7	16.802	100
200	18.597	42.7	18.423	16.7
021	19.523	14	19.362	12.1
121	21.595	18.8	21.444	28.8
211	22.623	11	22.474	12.1
310	29.244	47.9	29.072	19.7
301	29.623	65.9	29.517	28.8
132	33.482	23.4	33.337	13.6
321	34.225	13.7	34.103	13.6
041	35.467	58.5	35.252	31.8
410	38.489	12.9	38.338	21.2
104	40.335	13.3	40.226	27.3
114	41.364	10.8	41.181	4.5
402	42.504	12	42.357	7.6
124	43.980	17.7	43.841	16.7
134	48.537	21	47.064	9.1
342	48.938	16.2	48.822	7.6

to calcium-oxygen bonding. This spectrum is compared with the spectrum of calcium tartrate crystals prepared using AR grade tartaric acid. The observed vibrational frequency and their assignment are presented in Table 5. FTIR spectrum reveals the

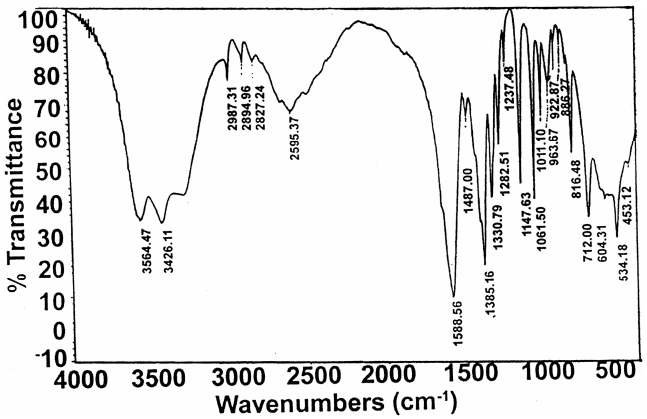


Fig. 5—FTIR spectrum of calcium tartrate crystals prepared from centrifuged tamarind juice

Table 4—Crystal data of calcium tartrate crystals

Molecular formula	$CaC_4H_4O_6\ 4H_2O$
Lattice parameter	a = 9.627 Å, b = 10.569 Å, c = 9.215 Å
	$\alpha = 90.00°$, $\beta = 90.00°$, $\Upsilon = 90.00°$
Molecular weight	260.21
Volume	937.61 $A^{0\ 3}$
Lattice	Orthorhombic
Space group	$P2_1\ 2_1\ 2_1$

presence of water molecules, O-H bonds, C-O bond and carbonyl C=O bonds.

From the spectrum, it was found that although the radiations are absorbed at same frequency in both the crystals, the percentage of transmittance of calcium tartrate crystals prepared from centrifuged tamarind juice is higher than that of crystals grown using AR grade tartaric acid. This may be due to the absence of IR absorbing impurities in centrifuged tamarind juice.

3.3 TGA and DTA studies of the grown calcium tartrate crystals

The analysis was performed from 28 to 625°C at a rate of 10°C/min. The thermal decomposition of the grown calcium tartrate crystals occurred in four stages between 88°C and 625°C. The TG and DTA curves are shown in Fig. 6.

In the DTA curve, there are three endothermic peaks at 113.18, 166 and 302.44°C and one exothermic peak at 468.84°C. The endothermic peaks at 113.18°C and 166°C are due to the decomposition of hydrated calcium tartrate into anhydrous calcium tartrate. The endothermic peak at 302.44°C is due to the decomposition of anhydrous calcium tartrate into calcium oxalate. The exothermic peak at 468.84°C is due to the decomposition of calcium oxalate. In this

Table 5—FTIR spectral data for calcium tartrate crystals

Band (cm^{-1})		
Calcium tartrate from centrifuged tartaric acid	Calcium tartrate from AR grade tartaric acid granules	Assignment
3564.47 (s)	3564 (S)	OH stretching
3426.11(s)	3426 (S)	OH stretch (water)
2987.31(m)	2988.1	CH stretch
1538.56(vs)	1589.0	C=O stretch
1385.16(vs)	1385.1	λ (C=O)+ δ(O-C=0)
1330.79(S)	1282.8	OH plane bending
1147.83(S)	1147.0	δ (C-H) +π (C-H)
1061.50(S)	1061.0	Out of plane OH deformation
1011.10(m)	1010.8	C-O stretching
963.67(m)	962.6 (s)	
922.87(w)	885.4 (m)	
886.27 (w)	816.9 (s)	Ca-O mode
816.48 (m)	711.8 (m)	
712.00 (s)	534.3 (m)	
604.31(s)		
534.18 (s)		

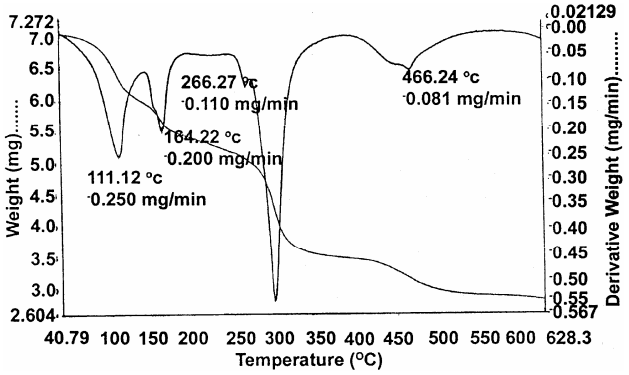


Fig. 6—TG and DTA curve for the calcium tartrate crystals

case, the final decomposition products are calcium oxide, calcium carbonate and carbon monoxide. Using calcium tartrate prepared from AR grade tartaric acid, the final decomposition product was calcium oxide. Comparing the present work with earlier studies, it is clear that the decomposition[2] is not completed at 625°C. Hence, higher temperature is required for the decomposition of calcium tartrate prepared using centrifuged tamarind juice into calcium oxide.

The calculated and observed values after degradation are presented in Table 6. When these

Table 6—Thermal degradation of the grown calcium tartrate crystals

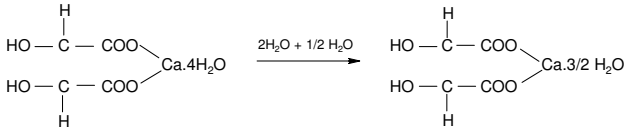
Range of mass loss		Mass loss observed (%)	Mass loss calculated (%)
DTA temp (°C)	TG temp (°C)		
113	88-154	16.7	17.33
166	160-289	13.6	13.8
302	300-427	21	21.15
468	430-510	8.9	8.5

values are compared with those of calcium tartrate prepared from AR grade tartaric acid, the mass loss observed, is found to differ. Hence, the expected stages of decomposition in the two cases are different. This may be due to the presence of other impurities in tamarind.

The expected scheme of decomposition might be as follows:

$$CaC_4H_4O_6.4H_2O \rightarrow CaC_4H_4O_6.4H_2O - (2H_2O+½H_2O) - (H_2O+½H_2O+½H_2O) - (H_2O+½H_2O+2C) - (½CO_2) \rightarrow ½CaCO_3 + ½CaO+CO$$

Stage I



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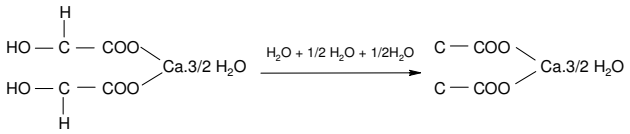

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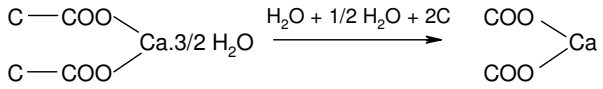
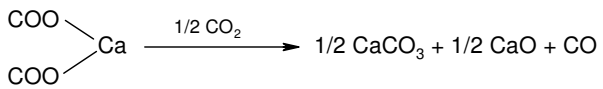


Stage IV



Thermal decomposition of calcium tartrate crystals prepared from AR grade tartaric acid (Table 7) is as follows:

$$CaC_4H_4O_6.4H_2O \rightarrow CaC_4H_4O_6.4H_2O$$
$$-(2H_2O+½H_2O)-(H_2O+½H_2O+½CO_2)$$
$$-(2CO+½CO+2H_2)-(½CO+ ½CO_2) \rightarrow CaO.$$

DT and TGA of both the samples were taken from room temperature to 625°C. In the case of calcium tartrate crystals prepared from AR grade tartaric acid, when the temperature reached 625°C, it has decomposed to calcium oxide. But in the case of calcium tartrate crystals grown from centrifuged tamarind juice, the crystal has not decomposed to calcium oxide at 625°C. The mass loss observed were found to be different in both the samples. From this, it can be concluded that the crystal grown from centrifuged tamarind juice is thermally more stable compared to the other.

3.4. CHN analysis of the grown calcium tartrate crystals

The powdered sample was subjected to C, H and N analysis using Elementar vario EL111 CHNS equipment. The result of this analysis is presented in Table 8.

3.5. AAS of the grown calcium tartrate crystals

The grown crystals were subjected to AAS studies. The concentrations of sodium, potassium and phosphorous were determined in order to check the degree of purity of the grown crystal. The result is presented in Table 9. This confirms the presence of other elements in the crystal. The difference in the mass loss observed in the DT and TGA data may be due to the presence of these elements.

Table 7—Thermal degradation of calcium tartrate crystals prepared from AR grade tartaric acid

Range of mass loss		Mass loss observed (%)	Mass loss calculated (%)
DTA temp (°C)	TG temp (°C)		
119	90-154	17	17.36
173	160-200	18	18.84
274	220-300	28	28.45
457	340-510	14	13.83

Table 8—C,H and N percentage in the grown crystal

Element	Observed value (%)	Calculated value (%)
N	0	0
C	18.74	18.5
H	5.29	4.6

Table 9—AAS data

Na	592 mg/kg
K	120 mg/kg
P	1500 mg/kg

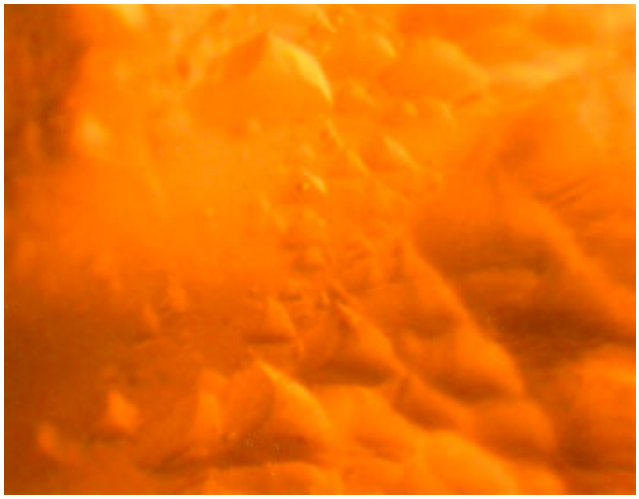


Fig. 7—Etched calcium tartrate crystal

3.6. Etching studies of the grown calcium tartrate crystals

Small, well defined calcium tartrate crystals were dipped in dilute nitric acid and was observed under optical microscope. The etched crystal is shown in Fig. 7. The morphology of the etch pits on the grown crystal is triangular which indicates that the plane is (111). It shows that the main growth direction is the (111) direction.

4. Results and Conclusion

Calcium tartrate tetrahydrate crystals were grown using crude tamarind juice as well as centrifuged tamarind juice in hydrosilic gel as medium. In this work, fresh tamarind fruits collected from tamarind tree were used. No similar work was found in the literature. The studies on the growth parameters of the crystal were conducted and it was observed that the gel of pH between 6.5 and 7.5 gives the best result. In order to obtain good quality, well faceted crystals, the concentration of supernatant solution (calcium chloride) should be 0.5 M. The density of sodium metasilicate should be 1.05 g/cc.

The characterization studies such as XRD, FTIR, TG, DTA, AAS, CHN analysis and etching studies were done. The results of XRD, FTIR, TG-DTA of the grown crystals were compared with that of calcium tartrate crystals grown from AR grade tartaric acid. From these studies, it can be concluded that the grown crystals are orthorhombic with lattice parameters a=9.627 Å, b=10.569 Å, c=9.215 Å, α=90.00°, β=90.00°, γ=90.00°, having greater thermal stability and having (111) direction as the main growth direction.

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