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Study of structural and physical properties of calcium tartrate crystals grown by single diffusion technique

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ABSTRACT

The fast development in the field of optoelectronics necessitates the search for new and efficient NLO crystal materials, which can be used for optoelectronics applications, such as optical computing, optical data storage, optical communication and electro optic shutters. For the fulfilment of these applications, crystals of calcium tartrate were grown by a simple gel technique using single diffusion method. The optimum growth conditions were established by various parameters such as pH of gel solution, gel concentration, gel setting time, concentration of reactants etc. Crystals having different morphologies and habits were obtained. The crystal size is about 5 x 4 x 3 mm. Calcium tartrate crystals are found to be orthorhombic with lattice parameters: a = 9.45900 Å, b = 6.46400Å, c = 5.39600Å. The crystals were characterized by using XRD, TGA and DTA techniques.

Keywords: Growth by single diffusion gel technique, XRD, TGA and DTA.

INTRODUCTION

Tartrate crystals are of considerable interest, particularly for basic studies of some of their interesting physical properties. 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 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 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 recent study, we have grown pure calcium tartrate tetra hydrate single crystals using calcium chloride mixed with tartaric acid as the supernatant solution [1-8]. The grown crystals have been characterized by XRD, TG and DTA studies.

MATERIALS AND METHODS

In the present work, the silica gel method was employed for the growth of calcium tartrate crystals. The crystallization apparatus used essentially consists of simple glass test tubes of length 25 cm and diameter 2.5 cm. Double distilled water was used for dilution, wherever required, throughout the study. Tartaric acid and calcium chloride solution were prepared by dissolving these compounds in an appropriate amount of distilled water to give the required morality.

Gels of required specific gravity were prepared by adding to the solution of sodium meta silicate, a calculated amount of redistilled water and a stock solution was kept ready for doing further experiments. Sodium meta silicate solution of a suitable specific gravity was taken in a 50 ml beaker and tartaric acid solution of particular strength

was added drop wise using a typhlon cock burette, constantly stirring the solution in the beaker by magnetic stirrer. Stirring is done to avoid the excessive local ion concentration, which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. The digital pH meter was used to measure the pH the solution. After measuring the pH value, this solution was gently poured into the test tube, being allowed to fall along the side of the test tube without giving chances for the formation of the bubbles. Test tubes were then closed with cotton to prevent evaporation and contamination of the exposed surface by dust particles of atmosphere.

The gel in the pH range 4 to 5 was usually found to set in 7 to 10 days, depending on the room temperature, after ensuring firm gel setting, the saturated solution of calcium chloride (supernatant) of particular strength was poured over the set gel with the help of a pipette. The solution is being allowed to fall along the wall of the test tube to prevents the gel surface from cracking. The supernatant solution slowly diffused in to the gel medium, where it reacts with the inner reactant, giving rise to the slow precipitation of $CaC_4H_4O_6$. [9-12]. The following reactions took place,

C4H6O6 + CaCl2 → CaC4H4O6 + 2HCl

Crystals of calcium tartrate are whitish, semitransparent and diamond shaped. Crystals having size 3mm x 4mm and thickness of about 2 to 3mm are obtained. Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel aging time etc. have considerable effect on growth rate.

Near the interface of gel, dendrite growth is observed due to fast growth rate. However as the reactants percolates through the gel, the controlled reaction occurs below, at the depth of 3 to 4 cm. Hence good quality, semitransparent, well developed faces of crystals are observed. This results due to the decrease in concentration of reactants at the depth of 3 to 4 cm below the gel interface. Table 1 gives the various optimum conditions for calcium tartrate crystals grown in silica gel.

Table 1 Optimum conditions for growth of Calcium tartrate

Sr. No	Optimum conditions	Calcium tartrate
1	Density of sodium meta silicate	1.04 gm/cm3
2	Concentration of tartaric acid	0.5M
3	Volume of tartaric acid	7ml
4	Volume of sodium meta silicate solution	17ml
5	Volume of Calcium Chloride	5ml
6	pH of the gel	4.2

In present work, figure 1 shows CaTr crystals in test tubes, figure 2 shows few whitish crystals outside the test tube and figure 3 shows photo graph of magnifying view of calcium tartrate grown under different conditions.

Fig 1 Calcium tartrate crystals inside test tube

Fig 2 Few crystals of Calcium tartrate out of test tube

Fig 3 (a) Magnifying view of Calcium tartrate crystal

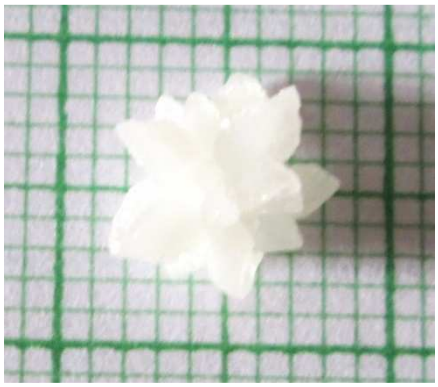

Fig 3 (b) Magnifying view of Calcium tartrate crystal

RESULTS AND DISCUSSION

Calcium tartrate crystals were characterized by XRD, TGA and DTA techniques.

XRD

X – Ray diffractogram was recorded using Rigaku Miniflex, Japan diffractometer with Cukα radiation (1.5418Å).The powder X- Ray diffractogram for pure calcium tartrate crystals is shown in figure 4. The observed 'd' values and hkl values were computed. The computer program POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program version 2.2) was used to calculate'd' values.

The observed peaks in diffractogram show that the calcium tartrate crystal possesses orthorhombic structure with lattice parameters: a = 9.45900 Å, b = 6.46400Å, c = 5.39600Å. The unit cell parameters of calcium tartrate crystals are shown in table 2. They are in good agreement with reported ones [13-15].

Table 2 Unit cell parameters

Sr.No	Parameter	$CaC_4H_4O_6$
1	System	Orthorhombic
2	A	9.45900Å
3	B	6.46400Å
4	C	5.39600Å
5	α=β=γ	90^0

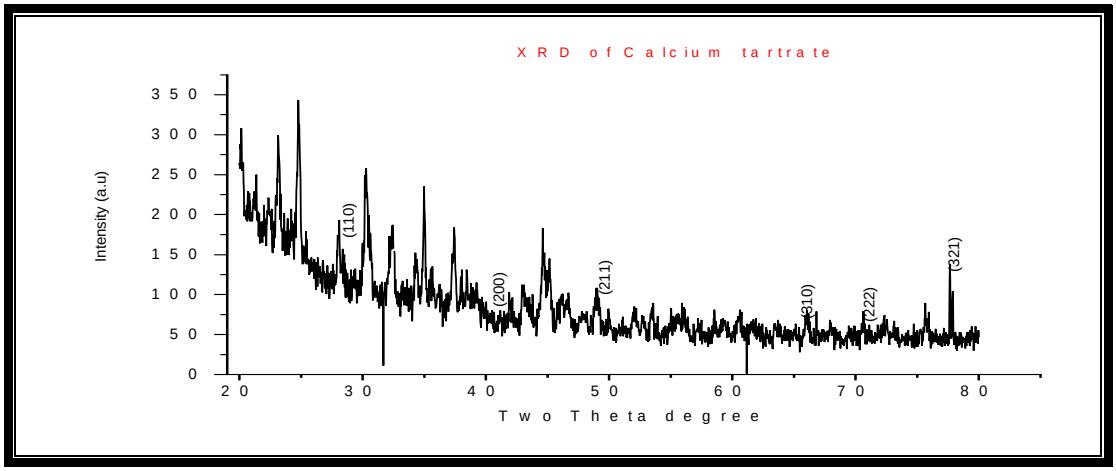

Fig 4 XRD of Calcium Tartrate crystal

THERMAL STUDIES OF CALCIUM TARTRATE CRYSTAL

The thermograms of calcium tartrate were obtained. Microcrystalline samples of CaTr crystal were taken for thermal studies and the weight of the sample was 3.4380 mg. The sample was hold for 1 min at 10^0c to evaporate water due to moisture and then heated from 30^0c to 1000^0c at the rate of 10^0C / minute. The TGA curve for gel grown CaTr is shown in figure 5. The percentage of the weight loss in the different stages of decomposition of CaTr is presented in table 3. There is a good agreement between the observed and calculated weight losses [16-17].

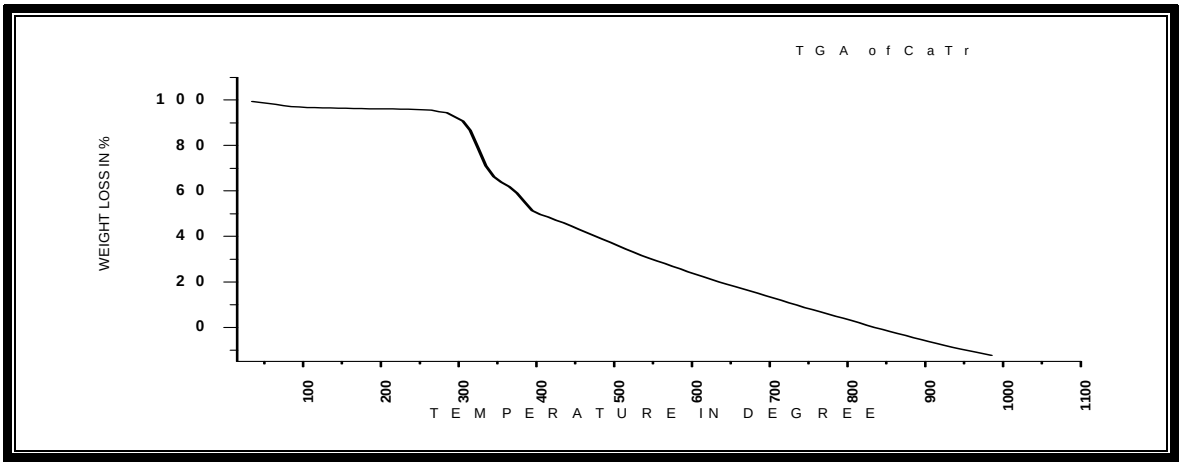

Fig 5 TGA of Calcium Tartrate Crystal

Table 3 Results of decomposition process of calcium tartrate crystals

Decomposition Step	Temperature range in ^{0}C	Observed weight loss in %	Calculated weight loss in %
I	45 - 160	3.432	3.427
II	180 - 330	29.56	29.49
III	375- 390	14.97	14.99
IV	400- 830	0.1534	0.1545

DTA

The DTA curve of calcium tartrate crystal grown by single diffusion is shown in figure 6 and the data collected from this curve is tabulated in table 4. It is observed that there are two endothermic peaks at 77.17^0C and 432.49^0C. The

endothermic peak corresponds to formation of calcium carbonate compound. One exothermic peak is observed at 492.39^{0}C.

Table 4 DTA data

No	Peak Temperature in ^{0}C	Nature of reaction
1	77.17	Endothermic
2	432.49	Endothermic
3	492.39	Exothermic

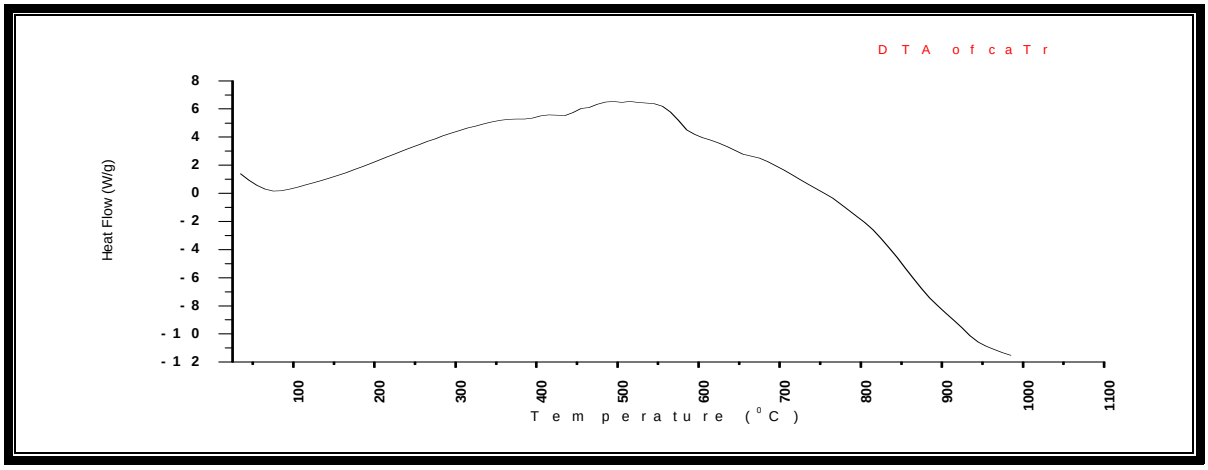

Fig 6 DTA curve of Calcium Tartrate

CONCLUSION

1) Calcium tartrate crystals can be grown in silica gel by single diffusion method.
2) Different habits of calcium tartrate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, concentration of reactants etc.
3) It was found that well developed single crystals of calcium tartrate are obtained at 1.0M concentration of feed solution in the pH range 4.2 to 4.4 of the gel.
4) The observed peaks of XRD show that the tartrate crystals possess orthorhombic structure
5) Thermal behaviour of the material reveals that decompositions take place through two exothermic stages and one endothermic stage.

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