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Studies on growth, thermal and dielectric behavior of calcium succinate trihydrate single crystals

M.P. Binitha, P.P. Pradyumnan*

Department of Physics, University of Calicut, Calicut University, PO, Malappuram 673635, Kerala, India

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ABSTRACT

Calcium succinate trihydrate crystals have been grown by gel aided solution growth technique and the effect of different growth parameters on the growth of the crystal is investigated. The compound is characterized by X-ray single crystal structure determinations and powder X-ray diffraction (XRD) technique. The thermogravimetric (TG), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) studies were carried out to investigate the thermal stability of the crystal. The dielectric behavior of the title compound crystal was investigated by measuring the dielectric constant and a c conductivity as a function of frequency at temperatures ranging from 30 °C to 110 °C.

1. Introduction

Single crystals have proved pivotal and indispensable in furthering research and delineating practical applications of solids, thereby contributing immensely to studies on technologically important materials. Current technological boom can be attributed to the innovation of single crystals which have accelerated and launched many theoretical speculations and generated techniques associated with it.

Succinic acid is a naturally occurring ligand present in many organisms [1]. It is an important intermediate in the tricarboxylic acid cycle and is used via reactions in the tricarboxylic cycle and glyoxylate cycle for the synthesis of amino acids and carbohydrates [2–4]. It activates the second half-cycle of tricarboxylic acids to help accelerate the decomposition of acetaldehyde and the energization of the oxidation processes in the mitochondria and hence plays major role in energy metabolism. It is also one of the fermentation end products of energy metabolism [5]. Succinates are the salts of succinic acid with two methylene groups between the carboxylic groups. Succinate is present, in free or bound form, especially as calcium and potassium succinates, in unripe fruits, algae, fungi, and lichens [6]. Succinates are used in the preparation of drugs and in flavorings [7,8]. It, as a bio-stimulant has been shown to stimulate neural system and recovery processes. In this paper we report the single crystal growth of calcium succinate trihydrate in hydro silica gel medium for the first time and explore its crystal structure. The studies on crystallization and characterization of calcium salts of carboxylic acids is having special significance in biochemistry because of the interactions of calcium ions with carboxylates in the blood and bone proteins containing the modified amino acid residues γ-carboxyglutamic acid and β-carboxyaspartic acid [9]. Details of thermal degradation and dielectric properties of the crystal is also studied and reported here.

2. Experimental

Single crystals of calcium succinate trihydrate were grown by ionic diffusion of calcium chloride in hydro-silica gel. The stock solution of desired specific gravity (ranging from 1.02 to 1.06) was prepared by dissolving appropriate quantity of sodium metasilicate powder in double distilled water. Succinic acid solution of particular strength (0.25 M to 1.5 M) was taken in a beaker and the stock solution is added to it drop by drop using a pipette. The stock solution is added until the pH of the gel is set at the desired value (between 3 and 7). Test tubes were then tightly closed to prevent evaporation and contamination of the exposed surface of the gel by dust particles from the atmosphere. The gel setting period varied from 1 to 6 days depending on the setting condition employed.

* Corresponding author.
E-mail addresses: binithamp@gmail.com (M.P. Binitha), drpradyumnan@gmail.com (P.P. Pradyumnan).

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The growth process was initiated by the diffusion of calcium chloride solution of molarity varying from 0.25 M to 1.5 M, which was introduced on the top of the set gel, without tampering the meniscus of the gel. The poured supernatant liquids diffuse slowly into the gel medium and react with the succinate ions and if the concentration of the diffusant is optimum or appropriate it will give rise to the slow and tiny precipitated nuclei of calcium succinate trihydrate ($CaC_4H_4O_4 \cdot 3H_2O$). The following equation represents the reaction responsible for crystal growth within the gel medium.

$$CaCl_2 + C_4H_6O_4 + 3H_2O \rightarrow CaC_4H_4O_4 \cdot 3H_2O + 2HCl$$

Well-developed crystals were separated from the gel medium after ensuring their maximum growth and structural characterization was performed using single crystal X-ray diffraction technique and X-ray powder diffraction technique. Single crystal X-ray diffraction data were collected using a Bruker Kappa Apex II diffractometer, with graphite- monochromator Mo-$K\alpha$ (λ=0.71073 Å) radiation. The unit cell dimensions were recorded at 296 K. Powder X-ray diffraction studies were carried out by Rigaku Miniflex 600 by Cu-$K\alpha$ monochromator of wavelength 1.541 Å. Thermo-analytical techniques such as TG, DTG and DTA were carried out using Perkin Elmer TGA instrument under nitrogen atmosphere at a heating rate of 10 °C/min. DSC analysis was done employing a Perkin Elmer DSC 4000 with a heat flow from 50 °C to 375 °C at 10 °C/min. The ac electrical conductivity measurements were done on the grown crystals in the temperature range of 30 °C to 110 °C using LCR meter (LCR Hi TESTER 3532-50).

3. Results and discussion

3.1. Growth kinetics

The effect of various growth parameters such as gel pH, gel density, gel age and concentration of reagents on the growth of calcium succinate trihydrate crystals were investigated by conducting separate experiments. Details of growth observations are discussed in the following session.

3.1.1. Effect of pH of the gel

The effect of pH of silica gel was studied using different ratios of sodium meta silicate and succinic acid in the mixture of silica gel. As the relative quantity of sodium meta silicate was increased in the mixture, pH values were increased and lead to poor formation of crystals. However at low pH values it was difficult to set the gel. When the pH values ranging from 3 to 7 were tried, it was observed that below a pH of 3.5, the gel was not set completely while above the pH of 6, the gel was set, but the transparency of the gel was decreased. It was observed that good results were obtained at 5 pH. In lower pH gels, when it takes longer time to set, more water will evaporate out of it causing an increase in gel density which in turn reduces the pore size and hence the rate of diffusion of Ca^{2+} ions through these pores. This result in decrease in the number of nucleation cites and hence the number of crystals formed [10,11].

3.1.2. Effect of gel density

Solutions of 1 M succinic acid impregnated silica gel of different densities (1.02 to 1.06) were prepared. It was noted that high density gels take lesser time to set and they are mechanically stronger than the lower density gels. But the transparency of the gel is found to decrease with increase in gel density. For the value of gel density much lower than 1.02, the gel is found to be mechanically weak since it takes long time to set and often the gel get ruptured before setting, hence not suitable for growth. After gelation, feed solution i.e. $CaCl_2$ of a particular concentration (1 M) was poured above the set gel. Then the crystal count was recorded after the growth was observed to have been completed. It was noted that the nucleation count increases steadily and uniformly with increase in gel density up to 1.04 and then decrease with gel density. When the density of the gel medium was very low, which is below 1.02, the fewer crystals grown are relatively larger in size but the soft gel gets incorporated into the crystal, resulting into a less perfect product. When the gel density was far above1.05, the grown crystals were contaminated with gel, opaque and ill defined and hence their quality was much reduced. Close linked pores in higher dense gels are not able to communicate and this results translucent to opaque gels. The decrease in nucleation density with increasing gel density above 1.05 is ascribed to smaller pore concentration and poor communication among the pores in the case of denser gels [12].

3.1.3. Effect of gel aging

Solutions of silica gel of specific gravity 1.03 were prepared with 1 M succinic acid. Then these solutions were transferred to the growth apparatus in fixed amount and allowed to set and then allowed to age for different periods (1–6 days). It was found that with aging time, set-gel transparency decreases. After required aging, 1 M $CaCl_2$ were poured above the set gel. The crystal count was noted, after completion of growth. It was observed that the number of crystals is found to decrease with aging time. When the gel gets aged, the pore size decreases making the diffusion of Ca^{2+} ions into the gel slower. This is due to the increased evaporation of water inside the gel system. The more the gel gets aged, the more will be the water evaporating out of it. This will cause the lack of ionic carriers in the channel of the gel framework. Also the shrinkage of pores will cause discontinuities in the channel in the gel. Both these effects reduce the rate of diffusion of calcium ions and hence the reaction velocity is lessened, resulting into decreased count, as observed [13].

3.1.4. Effect of concentration of $CaCl_2$

The concentration of reactants plays an important role in the growth of crystals. Once the gel density and pH is fixed, the nature of the growth of crystals will depend on the concentration of the reactants. Gels of specific gravity 1.03 acidified with 1 M succinic acid was allowed to set in a number of test tubes. Then 7 ml of $CaCl_2$, of different concentrations ranging from 0.25 M to 1.5 M was poured above the set gel and crystal count were recorded. It was found that on increasing the concentration of $CaCl_2$, the nucleation density increases. The increase in nucleation with increase in concentration is because of the enhanced availability and probability of Ca^{2+} ions to react with the $C_4H_4O_4^{2-}$ ions in the medium [14]. Good quality crystal is obtained at a concentration of 1.25 M $CaCl_2$ with gel density 1.03.

3.1.5. Effect of concentration of succinic acid

The concentration of succinic acid is varied from 0.25 M to 1.5 M and the corresponding changes in the variation of growth rate and growth features of calcium succinate crystals are noted. It is observed that number of crystals formed increases with the increase in concentration of succinic acid. Here also the effect of increasing the $C_4H_4O_4^{2-}$ ions causes an increase in the number of calcium succinate crystals formed.

The best transparent single crystals of calcium succinate of maximum size $8 \times 3 \times 3$ mm^3 have been obtained with the optimized values shown in Table 1. The growth set up and grown crystals are shown in Fig. 1.