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Nucleation and Growth of Lanthanum Tartrate Crystals in Silica Gel

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ABSTRACT

Lanthanum tartrate crystals were grown by single diffusion gel growth technique in a sodium metasilicate gel media at ambient temperature. The effect of various parameters like pH of the gel, gel density, concentration of reactants, gel ageing on the growth of these crystals was studied. The optimum conditions required for the growth of these crystals are worked out. Semitransparent spiky spherulites and dendrite crystals were obtained. An attempt has been made to explain growth mechanism.

Keyword: Gel growth, Lanthanum tartrate, Spherulitic crystals.

INTRODUCTION

The high standards of living enjoyed by citizens of every nation of the word would not be possible without the development of new materials. A series of pure and mixed crystals have been grown by several researchers with the aim of identifying new materials for practical and industrial purposes [1-5]. Single crystals are the backbone of the modern technological revolution. Compounds of tartaric acid find several practical applications in science and technology because of their interesting physical properties such as dielectric, ferroelectric, piezoelectric and non-linear optical properties [6-10]. The art of growing crystals in gel is not new for researchers because of its simplicity, inexpensiveness and crystals can be grown at ambient temperature. But the challenges and opportunities in understanding the growth features and morphology of grown crystal remain there. Crystals of great interest from both solid state sciences as well as technological point of view has been reported by many investigators using gel method.

Rare-earth materials have attracted considerable attention on account of their luminescent and magnetic properties [11]. Rare-earth tartrates bearing the general formula $R_2(C_4H_6O_6)_3.xH_20$ (R= Nd, Dy, Gd, La, Di, Pr, Sm, Y) have also been grown by the gel method using silica hydrogel as a medium of growth [12-18]. The studies on crystals of lanthanum tartrate grown in silica gel medium in pure form have already been reported [19]. But in the literature survey, to the best of our knowledge, there is no report on the systematic growth of lanthanum tartrate crystals. The present paper reports the results of the detailed studies made on nucleation and growth of these crystals as a function of gel parameters like the specific gravity of the gel, gel pH, concentration of tartaric acid, concentration of feed solution, gel age etc. Thus we intend to make a systematic study of variations in the growth features of these crystals.

MATERIALS AND METHODS

Lanthanum tartrate shows poor solubility in water hence it was thought worthwhile to grow such a kind of material by chemical reaction at controlled rate using gel method [20, 21]. The experiments pertaining to the growth of lanthanum tartrate crystals were conducted in borosilicate glass tubes of 2.5cm diameter and 20cm length. Gel was prepared by mixing sodium metasilicate solution of specific gravity $1.06gcm^{-3}$ with the desired concentration of tartaric acid (0.5M to 1.5M) which acted as a lower reactant. The solution was continuously stirred to avoid local ion concentration, which may cause premature local gelling and make the final solution inhomogeneous. The pH of the gel medium was adjusted between values of 3 to 5. The solution with the desired value of pH was then transferred to several glass tubes. The glass tubes were sealed with cotton material to prevent fast evaporation and contamination of the exposed surface of the gel and left for gelling. The gel setting time was found to be strongly dependent on pH and environmental temperature. It would take about 24h for the gel to set in summer (32–40^oC), where as it would take even 3-4days for the gel to set in winter (20–25^oC). After confirming the gel setting, an aqueous solution of lanthanum chloride (0.25M to 1.5M) was carefully poured along the walls of the tube with the help of pipette over the set gel, in order to avoid any gel breakage. The La^{+3} ions diffuse through the narrow pores of the gel to react with the tartrate ions ($C_4H_4O_6^{-2}$) present in the gel as lower reactant, giving rise to the formation of lanthanum tartrate crystals.

The following reaction is expected to take place in the gel medium.

$$LaCl_3 + 3(C_4H_6O_6) \rightarrow La_2 (C_4H_6O_6)_3 + 6HCl$$

Based on the various experiments conducted leading to pH of gel, gel density, concentration of upper reactant, concentration of lower reactant, gel ageing etc., the best controlling parameters which lead to the growth of good lanthanum tartrate crystals are given as follows. Gel pH = 4.2; gel density = $1.06gcm^{-3}$; gel ageing for 72h; concentration of lower reactant = 1M; Concentration of upper reactant =1M. The crystals were harvested in a month.

RESULTS AND DISCUSSION

Crystal growth

Table 1 gives a detailed summary of the experiments and results on morphology, nucleation density and size of lanthanum tartrate crystals grown in silica gel. The results in table 1 shows that single crystals of lanthanum tartrate grows at a gel pH of 4, 4.2, 4.4, and for a gel pH>4.6, the crystals attain spherulitic morphology.

As soon as the upper reactant ($LaCl_3$) is poured over the set gel containing tartrate ions, there is an instantaneous reaction between the La^{+3} and $C_4H_4O_6^{-2}$ ions resulting in the spontaneous formation of precipitate. It is observed that the strength of the precipitation depends profoundly on the gel pH, higher the pH, stronger is the precipitation (remaining parameters being the same). This strong precipitate formed at high pH (pH>4.4), blocks the diffusing sites of the gel pores. Due to this the value of supersaturation developed at different sites inside the gel becomes very low and may not be appropriate for the growth of single crystals even though there is release of HCl as byproduct which further reduces the effective value of the gel pH. On the other hand at low gel pH value, concentration of precipitants ions ($C_4H_4O_6^{-2}$) becomes low. Due to this desired supersaturation for the growth the growth of crystals may not result. However it was observed that nucleation density becomes very high and it puts limits on the size of the crystals. Thus high gel pH value (pH>4.6) as well as low pH value does not gives fruitful results.

Table 1. Details of experiments for the growth of lanthanum tartrate crystals

Experiment	Constant Parameter	Changing parameter	Result
Variation of pH	Top reactant = 1M Lower Reactant = 1M Gel age = 72h	Gel pH 3.4 3.6 3.8 4.0 4.2 4.4 4.6	Strength of precipitate formed at pH>4.4 is strong, Normal, spiky spherulites, dendritic, platelets crystals observed for pH between 4 to 4.4.
Variation of upper reactant concentration	Gel pH = 4.2 Lower Reactant = 1M Gel age = 72h	Con. of upper reactant 0.5 0.75 1.00 1.25 1.5	Length of precipitate formed is appreciable for concentration of 1M. Normal spherulites, coalesced crystals in all cases.
Variation of lower reactant concentration	Gel pH =4.2 Upper Reactant = 1M Gel age = 72h	Con. of upper reactant 0.5 0.75 1.00 1.25 1.5	Length of precipitate formed is appreciable for concentration of 1M. Normal spherulites, coalesced crystals in all cases.
Variation of gel ageing	Gel pH =4.2 Lower Reactant = 1M Upper Reactant = 1M	Gel ageing 48 72 92 120 148	Nucleation density is high for low aged gel and low for high aged gel. The best ageing time was 72h, Normal spherulites, coalesced crystals in all cases.

In our experiments intermediate value of gel pH (4 to 4.2) is interesting. For this gel pH value, the precipitate formed at the solution-gel interface is neither strong nor weak. Under the optimum conditions established in series of experiments as explained earlier, the crystals of lanthanum tartrate are observed to grow basically in three zones of the gel medium. First zone is the interface between the gel and feed solution where instantaneous reaction between upper and lower reactant takes place resulting in the formation of crust. The crust is observed be poor quality microcrystallites. The second zone is the precipitate zone where crystals tend to grow out of precipitate. The precipitate formation at the gel reactant interface starts immediately after pouring the upper reactant solution. After attaining some thickness, the precipitate column advances into the gel leaving the clear gel in upper zone. Both upper as well as lower end of precipitate column advances into the gel, but the rate of advancement of lower end is relatively faster than upper end. The advancement of precipitate column continues for 10 to 15 days and attains the maximum size. At this stage further advancement of the precipitate column stops and usually stations itself somewhere in the middle of the gel column. The rate of advancement and maximum length of the gel column is found to depend on the upper reactant concentration. Table II gives the dependence of length of precipitate column on concentration of upper reactant.

Table 2 Length of precipitate column for different concentration of upper reactant

Concentration of Upper reactant (M)	Length of stationary precipitate (cm)
0.25	0.5
0.50	1.2
0.75	1.8
1.00	2.9
1.25	3.2
1.50	3.2
1.75	3.3

[Constant parameters: 1.Concentration of upper reactant = 1.0M, 2. pH of gel = 4.2 3. Density of gel = 1.06g cm$^{-3,}$ *4. Gel ageing = 72h]*

The explanation for the growth of crystals out of precipitate is based on the adsorption property of the gel and its dependence on pH [22]. This type of growth has been reported for barium and lead tartrate [23], didymium tartrate [14], praseodymium tartrate [16]. Silica gel is a polymerized form of silicic acid. It has a little role to play in crystal growth. Because of high rate reaction between reactants, the product i.e lanthanum tartrate has no time for regular growth into crystals. As a result of this, the formation of a colloidal precipitate takes place. With the continuation of reaction, more and more acid is liberated, which decreases the effective value of pH around the reaction site. In this zone spiky spheulites and crystal aggregates are observed to grow.

The peculiarity of crystal growth in this zone is that nucleating center is associated with a halo. Halo is a spherical region which is depleted of the colloidal particles. The halo increases with increase in crystal size. All crystal growing in this zone are associated with halo. Further it is observed that these halos merge into each other as many crystals grows.

The third zone is the bottom portion of the gel column where crystallization of lanthanum tartrate takes place without the intermediate step of precipitate formation. In this zone crystals develop without the formation of precipitate and keeping the gel visibly clear. The factors such as the smaller concentration gradient, steady diffusion and relatively stable pH, contribute to the growth of good quality crystals. Figure 1 shows the crystals of lanthanum tartrate growing in different zones of gel column under different growth conditions.

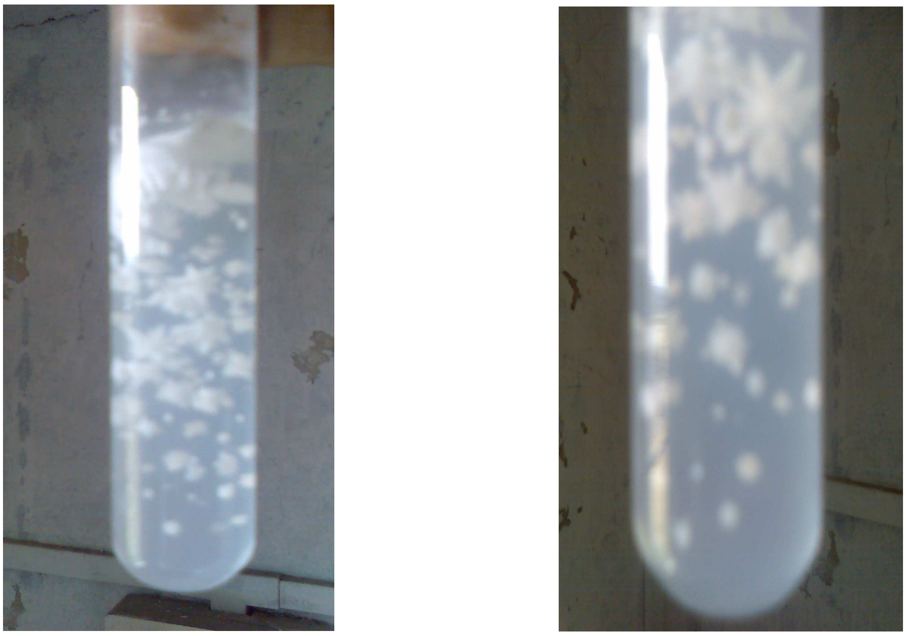

(a) (b)

Figure 1. Optical photograph showing growth of lanthanum tartrate crystals in different zones of gel column at different conditions (a) pH = 4 (b) pH=4.2

Cracking of the gel

During the preparation of the gel, dropping of the supernatant solution over the set gel or handling of the test tubes for many times may crack the gel. If such as crack develops, it acts as drainage cannel for the top reactant and top reactant percolates through these cannels resulting in the instantaneous formation of crystals on its way. The crystals formed in these cannels are similar to those obtained in the immediate vicinity of the gel-reactant interface (i.e. crust formation). Figure 2 shows the formation of crystals along the channels of cracked gel. The observations reported here are identical to the one reported by Kotru *et al*. [14, 15].

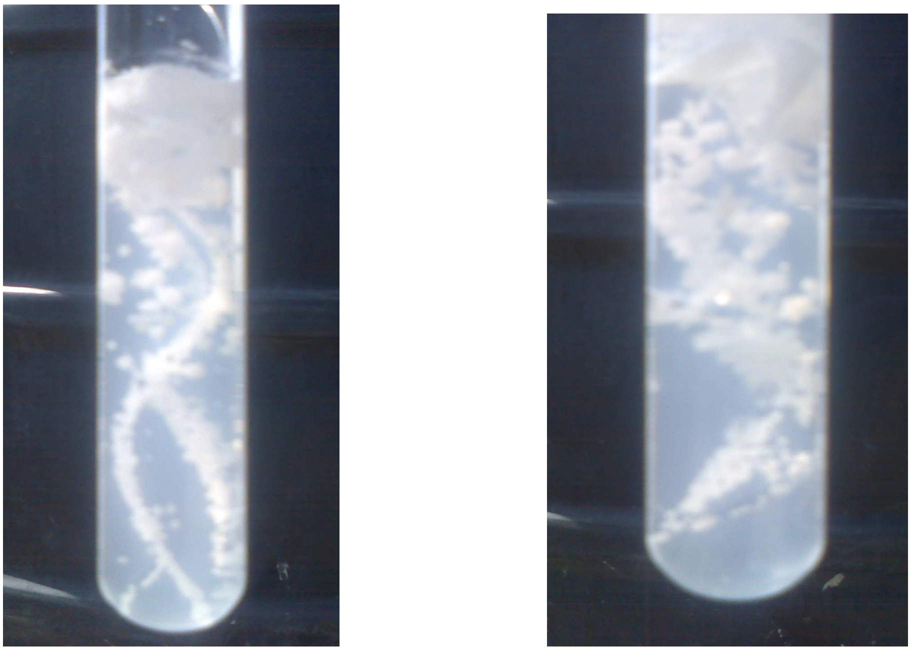
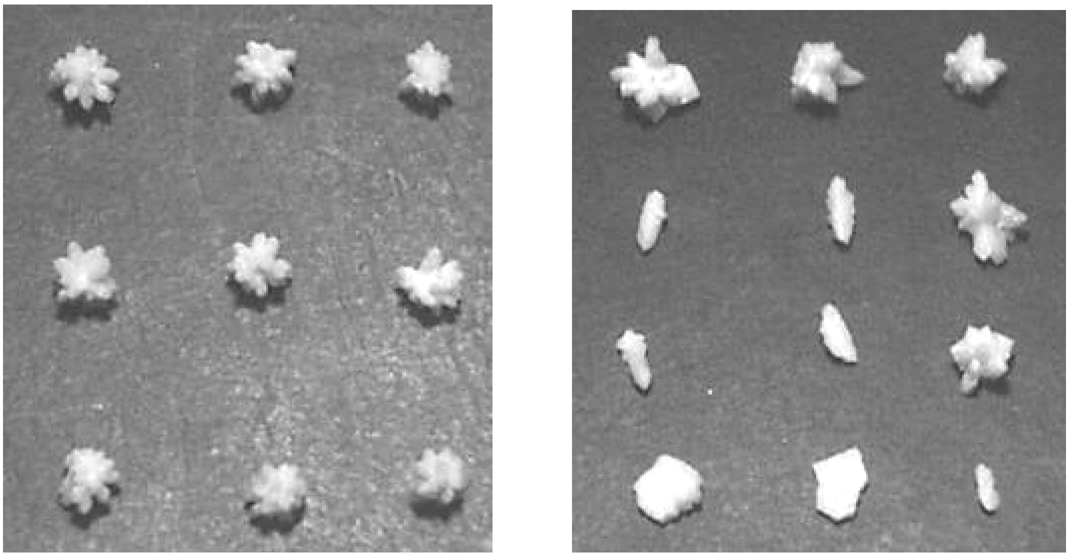

(a) (b)

Figure 2. Formation of lanthanum tartrate crystals along channels of cracked gel.

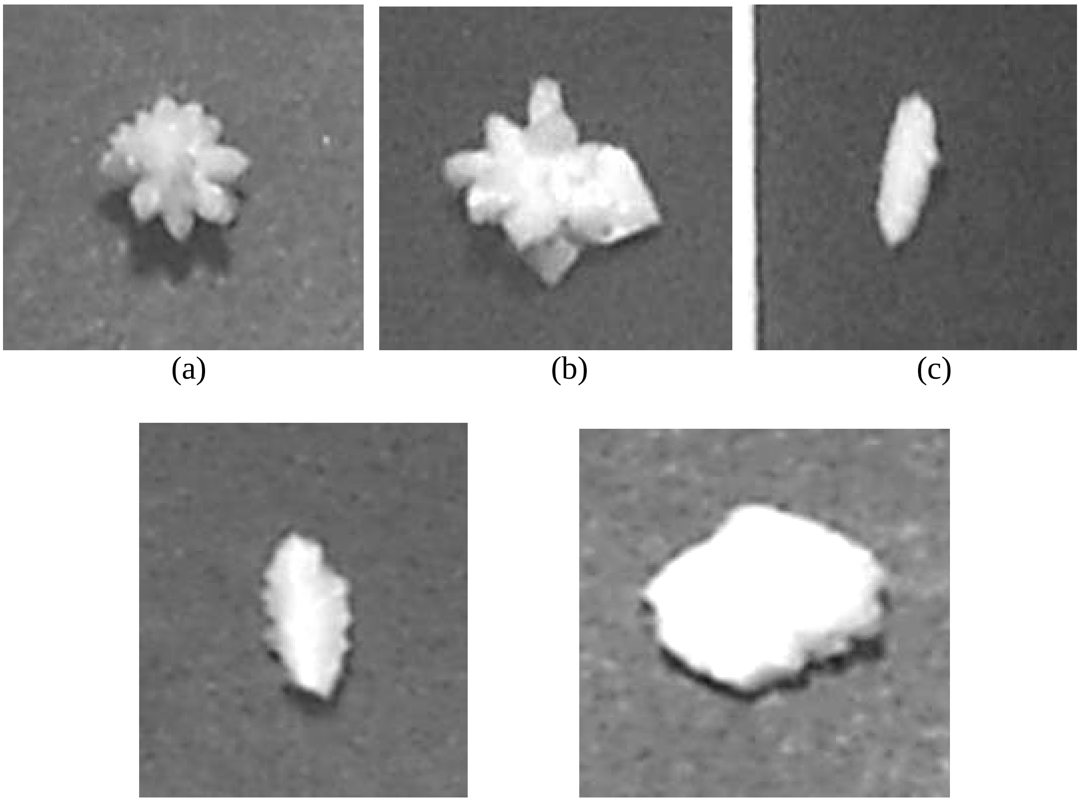
Morphology

Figure 3 illustrates different morphologies of pure lanthanum tartrate crystals grown under different conditions of growth. The crystals grown are spiky spherulites, multi-arm dendrites and rectangular platelets. Figure 4 shows enlarged photographs of some selected morphologies of grown crystals.



(a) (b)

Figure 3. Optical photograph illustrating varied morphology of lanthanum tartrate crystals grown under different growth conditions.



(a) (b) (c)

(d) (e)

Figure 4. Enlarged view of some selected morphology of grown crystals.

CONCLUSIONS

In view of the above observations, we may conclude the following;

1.The gel growth system can be successfully used for the growth of pure lanthanum tartrate crystals.

2.The diffusion of La^{+3} ions through the narrow pores of the silica lead to reaction between these ions and the $C_4H_4O_6^{-2}$ ions present in the gel as lower reactant. A good crop of crystals are obtained with the optimized parameters such as; Gel pH = 4.2; gel density = $1.06gcm^{-3}$; gel ageing for 72h; concentration of lower reactant = 1M; Concentration of upper reactant =1M.

3.Grown crystals exhibit varied morphology such as spiky spherulites, multi-arm dendrites and rectangular platelets.

4.Crystallization of lanthanum tartrate crystals takes place in three distinct zones. One is at the gel-reactant interface, the second is at middle precipitate zone where crystallization takes place out of precipitate and third is clear zone where crystallization takes place without intermediate step of precipitate formation.

5.The adsorption property of a gel pays an important role during the crystallization of lanthanum tartrate crystals.

6.The instant reaction between the two reactants at the gel-reactant interface leads to the formation of a crust whose building blocks are tiny crystallites.

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