

Growth of lanthanum tartrate crystals in silica gel

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The spherulitic, dendritic and single-crystal growth of hydrated lanthanum tartrate by controlled diffusion in silica gels is reported. The influence of growth parameters, e.g. reactant concentrations, gel pH, gel ageing, on the size and nucleation density of crystals has been studied. Operative mechanisms of crystallization, results of growth kinetics and morphology of crystals are discussed. The adsorption property of the gel is found to play a vital role during the crystallization of lanthanum tartrate crystals. Parabolic kinetics, characteristic of a one-dimensional diffusion-controlled process, for single crystals is observed to be obeyed in case of variation of upper reactant concentration.

1. Introduction

Crystal growth in gels has made remarkable progress in the recent years. With the advent of extensive work by Henisch and co-workers [1, 2], gel growth research made rapid strides in the field of crystal growth in general, and the growth of materials in gel in particular. The importance of gel growth can be visualized by the fact that a number of researchers have started to develop crystals of technological potential by this method [3-8]. Another factor arousing interest in this type of growth is the fact that crystals of various sorts, ionic, organic and even metallic, could be grown at ambient temperatures. Growth kinetics which is so vital in understanding the growth mechanisms involved in this type of growth has also been dealt with extensively [1, 9-12].

It is pertinent to point out here that, so far, essentially no work has been reported on the gel growth of rare-earth tartrates. For a long time now rare-earth compounds have been recognized for their magnetic and luminescent properties. We report here the growth of lanthanum tartrate in a gel medium. Certain aspects of growth, i.e. growth mechanism, growth kinetics and morphology of the grown crystals, are described and discussed.

2. Experimental procedure

The silica gel (acidified sodium metasilicate) was used as the growth medium throughout this study. All experiments carried out here were by the single-tube diffusion method. The double-tube diffusion method proved futile as no evidence of crystallization could be obtained. The tube employed was 2.5 cm in diameter and 20 cm long. The crystal growth process involves the diffusion of lanthanum nitrate (or lanthanum chloride) into the gel (specific gravity = 1.05 g cm⁻³) impregnated with tartaric acid. The following reactions are expected to take place in the gel medium.

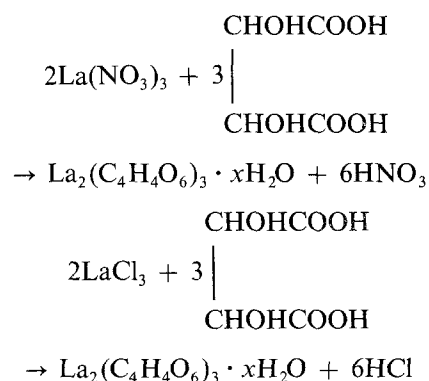


Table I gives a summary of the experiments and subsequent results obtained in the case of each of the experiments. All experiments were performed at room temperature.

A metallurgical microscope, Neophot-2 of Carl Zeiss, Germany, was used for observing crystals under a macro-illuminator.

3. Results and discussion

3.1. Mechanism of crystallization

The experiments carried out to study the growth mechanism associated with the growth of lanthanum tartrate crystals were performed using either lanthanum chloride or lanthanum nitrate as the upper reactant. Both were found to yield similar results in respect of the mechanism of crystallization, morphology or growth kinetics. Therefore, it will be sufficient to describe the results obtained from one of these reactants.

For the sake of clarity, the mode of crystallization will be discussed on the basis of three zones, where distinct mechanisms of crystallization become operative. The first is in the immediate vicinity of the gel-reactant interface. Here, on pouring lanthanum nitrate solution on to the top of the gel impregnated with tartaric acid, there is a spontaneous formation of crust as a result of an instantaneous reaction between the upper and lower reactants. The crust is observed to be

TABLE I Details of experiments for the growth of lanthanum tartrate

Experiments	Constant parameters	Changing parameter	Results
1. Variation of upper reactant concentration	Lower reactant (tartaric acid) concentration, 0.5 M Gel density, 1.05 g cm ⁻³ pH of gel, 4.5 Gel ageing, 24 h	Lanthanum nitrate (upper reactant concentrations) 1.00 M 0.75 M 0.50 M 0.25 M	Morphology: spherulitic, dendritic and single rectangular crystal platelets. Max. size of single crystal: 8 mm at 0.5 M Nucleation density, min. at 0.5 M, max. at 0.25 M
2. Variation of lower reactant concentration	Upper reactant (lanthanum nitrate) concentration, 0.5 M Gel density, 1.05 g cm ⁻³ pH of gel, 4.5 Gel ageing, 24 h	Tartaric acid (lower reactant concentrations) 1.00 M 0.75 M 0.50 M 0.25 M	Morphology: spherulitic, dendritic and single rectangular crystal platelets. Max. size of single crystal: 7 mm at 0.75 M Nucleation density, min. at 0.75 M, max. at 1 M
3. Variation of gel ageing	Upper reactant (lanthanum nitrate) concentration, 0.5 M Lower reactant (tartaric acid) concentration, 0.75 M Gel density, 1.05 g cm ⁻³ pH of gel, 5	Gel ageing 24 h 36 h 48 h 60 h	Morphology: spherulitic, dendritic and single rectangular crystal platelets. Max. size of single crystal, 6 mm at 60 h Nucleation density, max. at 24 h, min. at 60 h
4. Variation of gel pH	Upper reactant (lanthanum nitrate) concentration, 0.5 M Lower reactant (tartaric acid) concentration, 0.75 M Gel density, 1.05 g cm ⁻³ Gel ageing, 24 h	Gel pH 4.0 4.5 5.0 5.5	Morphology: spherulitic dendritic, and single crystal rectangular platelets. Max. size of single crystal, 6 mm at pH 5 Nucleation density, max. at pH 5, min. at pH 5

an agglomeration of poor quality micro-crystallites, the gel having little role to play, in so far as restriction of the diffusion of ions is concerned.

The second operative mechanism is the crystallization of lanthanum tartrate out of the precipitate. The precipitate is formed almost at the gel-reactant interface. After attaining some thickness the precipitate begins to advance into the gel. Both the upper, as well as lower, fronts of the precipitate advance, but the rate of advancement of the lower front of the precipitate is relatively faster, compared to that of the upper front, consequently leading to the growth of a precipitate column. The advancement of the precipitate continues for a number of days until some particular size is reached. At this stage, further advancement of the precipitate into the gel stops. The precipitate zone invariably becomes positioned almost in the middle of the gel column.

Table II gives the rate of advancement of the upper and lower fronts of the precipitate column for different concentrations of the upper reactant. The length of colloidal precipitate column is observed to increase with increase in concentration of the upper reactant, as is clearly indicated in the Table. Fig. 1 shows the precipitate column after it has ceased to move into the gel. The pattern of advancement of the precipitate is found to be the same for all concentrations (whether the upper reactant is lanthanum nitrate or lanthanum chloride). However, the total length of the precipitate column and the rate of its advancement into the gel is dependent upon reactant concentration, the total length being greater for higher concentration.

The precipitate phenomenon can be explained on the basis of adsorption and its dependence on pH [13]. This type of phenomenon has been reported by

TABLE II Rate of advancement of colloidal precipitate in the gel column

Tube no.	Concentration of lanthanum nitrate (M)	Period of advancement of precipitate (h)	Reading of precipitate boundaries from gel-reactant interface		Observed length of gel column (cm)	Rate of advancement	
			Upper boundary (cm)	Lower boundary (cm)		Upper boundary (10 ⁻³ cm h ⁻¹)	Lower boundary (10 ⁻³ cm h ⁻¹)
1.	0.5	435	1.1	3.0	2.9	2.528	6.896
2.	0.25	435	1.2	3.3	2.1	2.758	7.586
3.	0.1	435	1.0	2.1	1.1	2.298	4.827
4.	0.05	435	1.0	1.7	0.7	2.298	3.908

Constant parameters:

1. Concentration of lower reactant (tartaric acid) = 0.50 M.
2. pH of gel = 4.
3. Density of gel = 1.05 g cm⁻³.
4. Gel ageing = 24 h.

Changing parameter: upper reactant (lanthanum nitrate) concentration.

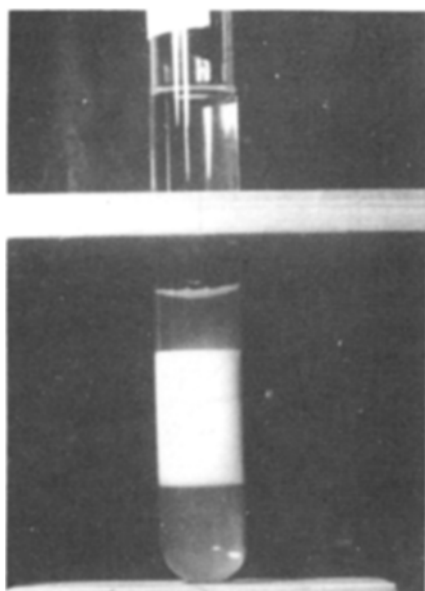


Figure 1. Colloidal precipitate column stationary in the gel column. Notice the crust formation at the gel-reactant interface.

Abdulkhadar and Ittyachen [14] for barium and lead tartrate crystals. Silica gel is a polymerized form of silicic acid. Because of the high rate of reaction of the reactants, the product of the reaction, i.e. lanthanum tartrate, has no time for regular growth into crystals. As a result of this they are precipitated into a colloidal conglomeration. The colloidal particles become adsorbed by the gel, resulting in a column of white precipitate. As the reaction proceeds, i.e. as lanthanum nitrate diffuses further into the gel, more and more acid is liberated. With the liberation of the acid, the effective value of pH decreases around the reaction site and the force of adsorption decreases with decrease in pH.

Two types of adsorption are worth considering: (i) adsorption of the colloidal particles by the gel, (ii) adsorption among the colloidal particles. When the top reactant (lanthanum nitrate) diffuses into the gel, the precipitate formed somewhere at the gel-solution

interface gradually attains thickness, the material in this band being colloidal particles of lanthanum tartrate. When a certain amount of nutrient has reacted, the acid liberated would reduce the force of type (i) adsorption to a minimum, if not zero; hence the colloidal particles move as a band downwards where pH of the gel and the consequent force of adsorption is large. In this way the thickness of the precipitate continues to increase as the colloidal particles of lanthanum tartrate roll along in the gel. As the reaction proceeds further, a stage will be reached where the pH of the gel around the band is reduced to a value where type (ii) adsorption decreases to a minimum, rendering the colloidal particles free. At this stage, the colloidal particles diffuse into the growth sites and the crystals start to grow. Figs. 2a to c show three tubes of growing lanthanum tartrate crystals. It is noticeable that in the upper portion (within the precipitate zone) the formation of crystals takes place in the form of spheres, twinned crystals and dendrites. This can be attributed to the presence of too many nuclei and the variation of effective value of pH within the precipitate zone. The lower portion of the tube depicts single crystals growing outside the precipitate zone.

The second mechanism which becomes operative for the crystallization of lanthanum tartrate in the precipitate zone has distinct features of its own. Soon after attaining stability in size and position over a week or so, nucleation of crystals start. Each nucleation centre is found to be associated with a halo, i.e. a spherical region in which the gel is depleted of colloidal particles. The halo is many times bigger than the centrally located nucleation centre and is filled with a clear solution resulting in transparency within it. The halo grows as the crystal grows. Fig. 3a shows a crystal just nucleated within the halo. After attaining a particular size the halo shows complete transparency as can be seen in Fig. 3b. Fig. 3c shows a case where more than one nucleus in close proximity give rise to haloes, which in the course of time merge into each other. The process continues until the whole precipitate in the gel

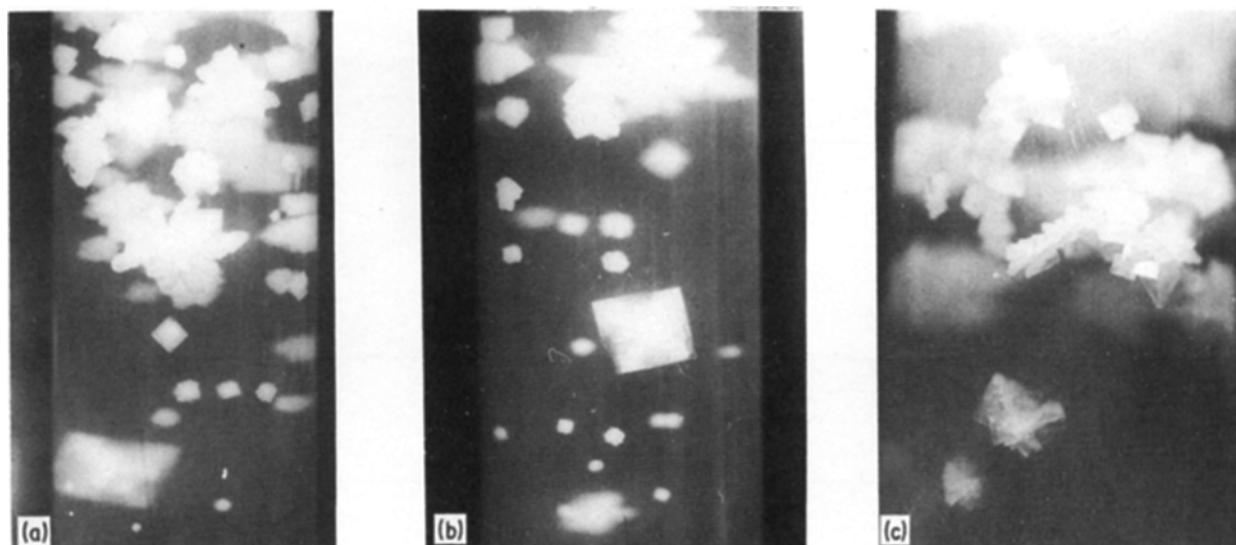


Figure 2 Crystals of lanthanum tartrate growing in the gel medium. Spherulitic, twinned and dendritic growth is predominant in the upper (precipitate) zone. (a) System showing multi-armed dendrites growing in the upper (precipitate) zone. (b) A large crystal of lanthanum tartrate growing in the lower zone of gel column. (c) Predominance of single-armed dendritic growth. Notice growth of twinned crystals also.

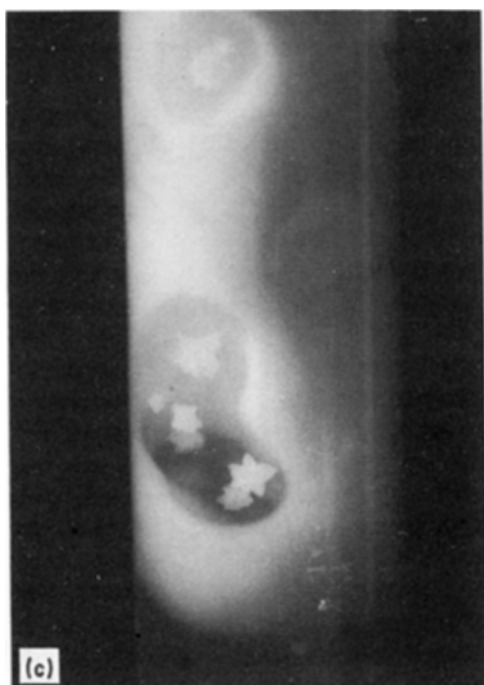
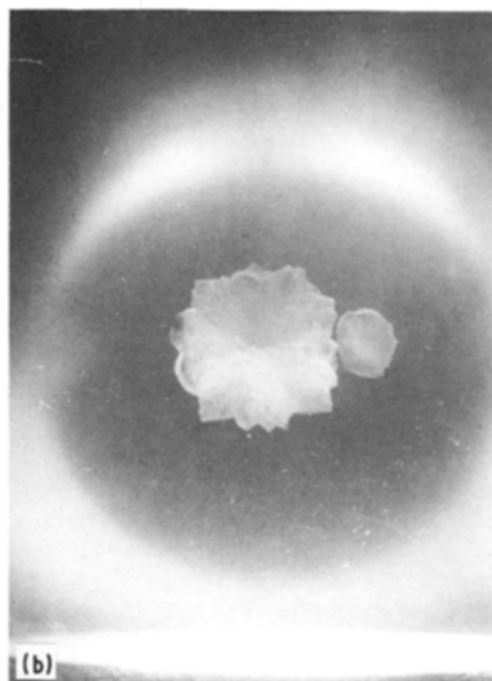
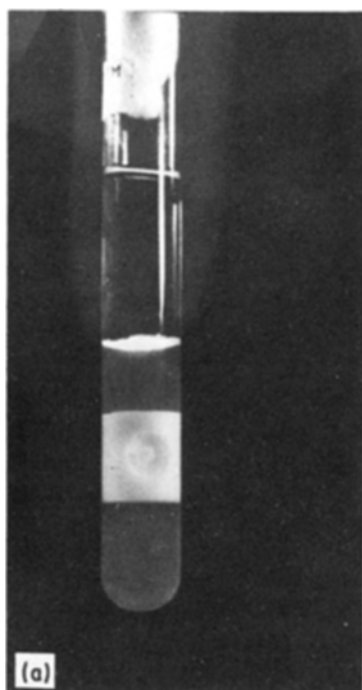


Figure 3 Crystals of lanthanum tartrate growing out of the colloidal precipitate after its advancement into the gel column ceases. (a) Nucleation of lanthanum tartrate crystal out of the precipitate, creating a halo. (b) A close-up photograph of apparently a sun flower-like crystal and a spherulite of lanthanum tartrate growing within the halo of much larger diameter than the growing crystal. (c) Several nucleating centres within the precipitate in close proximity, giving rise to haloes merged together. Notice growth also outside the precipitate (lower) zone.

column is dissolved, leading to a clear zone full of crystals.

The number of molecules required to build up a crystal (condensed matter) would be dispersed in a volume several times greater than the volume occupied by the crystal. The colloidal particles surrounding the crystal nucleation centre tend to migrate radially towards it from all directions. In this way, a spherical region of far greater volume than that of the growing crystal is depleted of colloidal particles, rendering the surrounding space clear from any precipitate, and thus the formation of a halo results.

The difference between this phenomenon observed in our case and that observed by Henisch [2] is, that while in the former the crystal grows within a halo, in the latter case the crystal is associated with a cusp. The type of cusp observed by Henisch has also been observed by Hanoka [15] and Joshi and Antony [16].

The third zone where the crystallization of lanthanum tartrate takes place is that where there is no precipitate formation. This zone is usually at the bottom below the precipitate zone. Here the crystals develop in the clear parts of the gel column from the very beginning, without formation of any precipitate. Crystals which develop in this zone are usually single crystals of much better quality. No dendritic growth is observed in this zone. This may be because of factors such as lower concentration gradients and relatively more stable pH in the lower zone and also because the crystals developing in this zone are formed in a gel relatively older than that above it.

4.2. Growth kinetics

Fig. 4 shows a graph of the length of the crystals plotted against the growth time for different concentrations of the top reactant (lanthanum nitrate). Other parameters which are maintained at constant value are also given in the figure. The figure shows evidence of parabolic characteristics of the growth rate. When, for the same conditions, a graph is plotted of l^2 against t , the pattern obtained is a straight line, as seen in Fig. 5. The maximum size of the crystal, i.e. 8 mm, is obtained in the case of 0.50 M lanthanum nitrate.

4.3. Effect of cracking of the gel

For any fault, either in the preparation of the gel or dropping of supernatant solution from above, the gel

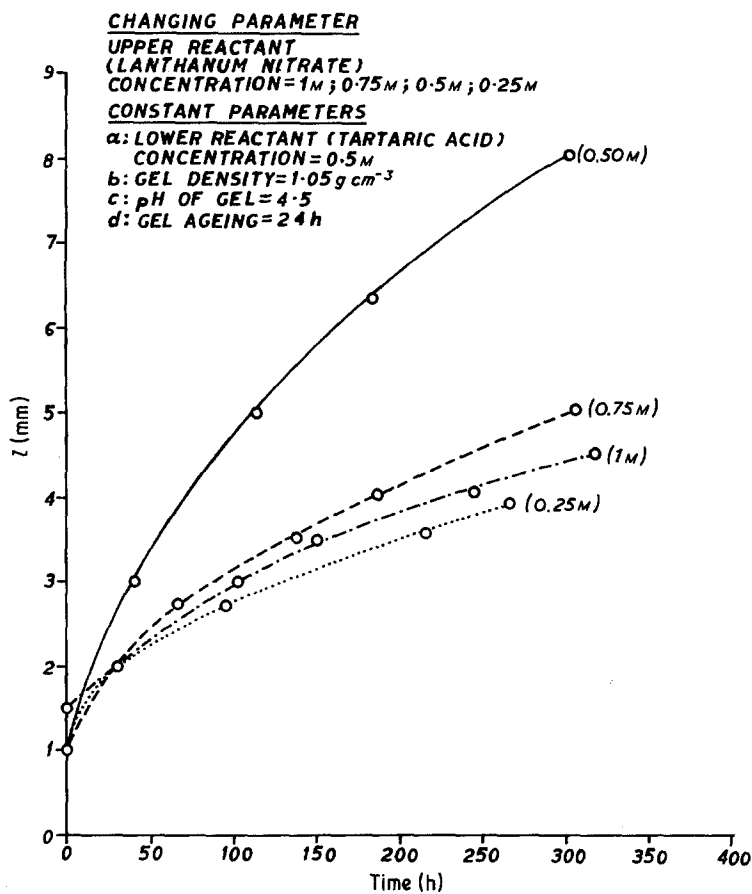


Figure 4 Graph showing dependence of length (l) of the crystal on time (t) of growth for different concentrations of the upper reactant (lanthanum nitrate).

may tend to crack any time during the operation of a growth system. If such a crack develops it acts as a drainage channel for the top reactant, as a result of which the reactant almost runs through the system resulting in instantaneous formation of crystals on its way. Such crystals are identical to those obtained in the immediate vicinity of the gel-reactant interface (i.e. crust formation). Fig. 6 shows an isolated case of this type where very small crystals having developed

along a curved channel (where the gel has cracked), are observed. This negates the advantages of using gel.

4.4. Morphology

Lanthanum tartrate crystals grown from silica gels exhibit varied morphology. The crystals grown are in the form of spherulites, single- as well as multi-arm dendrites, and rectangular platelets. Spherulitic growth is predominant in commercial (impure) silica

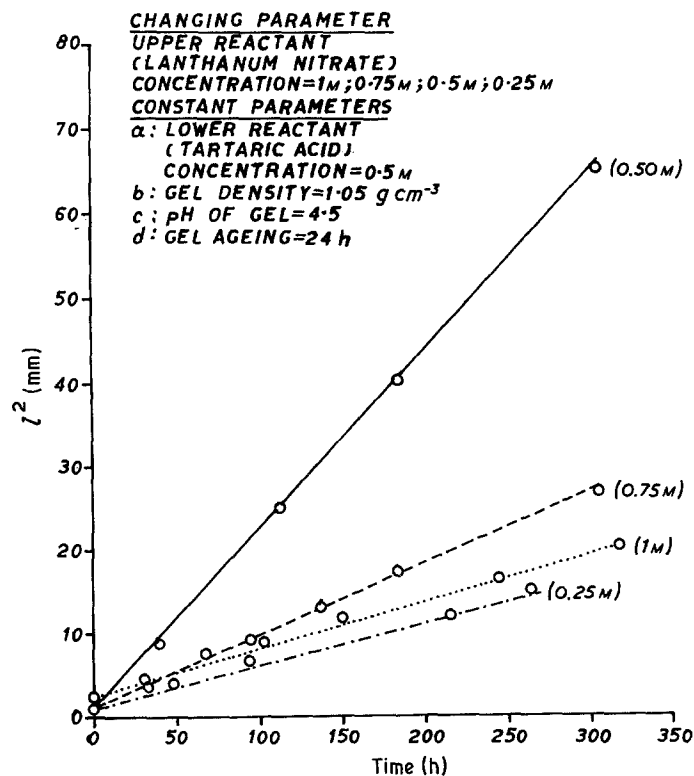


Figure 5 A plot of l^2 against t for different concentrations of the top reactant (lanthanum nitrate).

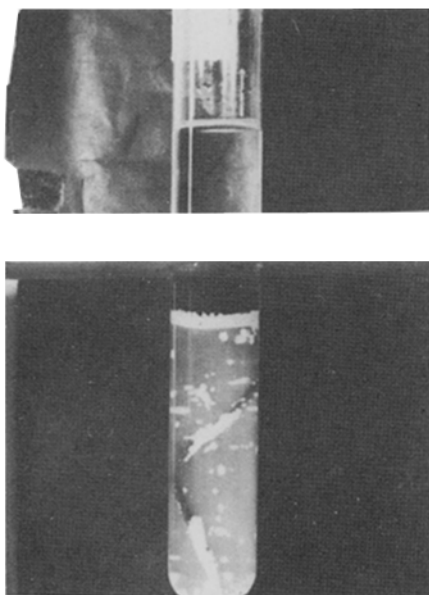


Figure 6 A curved channel, along the route where the gel has cracked, draining the nutrient and allowing instantaneous formation of crystals similar to the crust formation at the gel–reactant interface.

gel. However, crystals with spherulitic morphology are considerably reduced in the centrifuged gels, and are of a much improved quality. The spherulitic morphology as obtained in a centrifuged gel is shown in Fig. 7.

Crust formation in the immediate vicinity of the gel interface is the agglomeration of micro-crystallites as shown in Fig. 8.

The crystals developed out of the precipitate are mostly in the form of dendrites. For example, single- as well as multi-arm dendrites growing in the gel system are shown in Fig. 9. A clump of crystals with multi-arm dendrite growth morphology is shown in Fig. 10, and a dendritic growth with one-arm predominant is shown in Fig. 11. It is clearly seen in Figs. 10 and 11 that each dendritic arm is composed of inter-grown platelets. A lone crystal which mostly develops in the clear regions of the growth system is found to be a rectangular platelet.

5. Conclusions

1. Growth of lanthanum tartrate crystals is accomplished by allowing diffusion of lanthanum

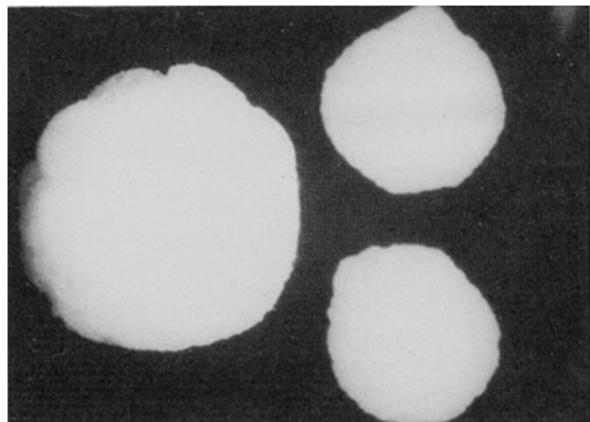


Figure 7 Spherulitic morphology of lanthanum tartrate, grown in the centrifuged gel, as seen under a macro-illuminator ($\times 8.5$).

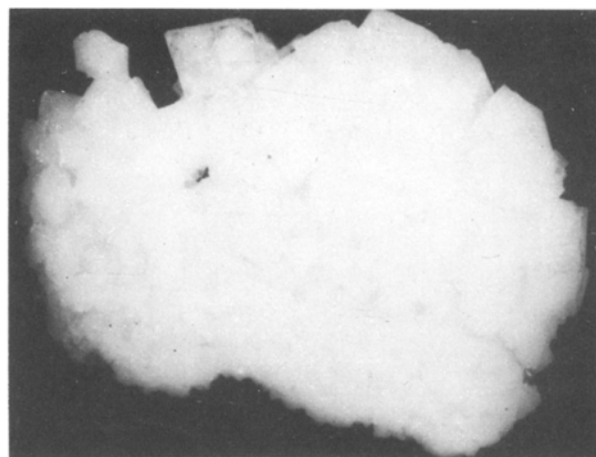


Figure 8 The crust formation at the gel–reactant interface as seen under a macro-illuminator, showing it as an agglomeration of micro-crystals ($\times 8.5$).

nitrate or lanthanum chloride through silica gel impregnated with tartaric acid.

2. Three distinct mechanisms of crystallization of lanthanum tartrate are operative. One as a result of the instantaneous reaction at the gel–reactant interface, the second involving nucleation and growth from the colloidal precipitate, and the third involving interaction of reactants in the clear zone without any intermediate step of precipitate formation.

3. The adsorption property of a gel plays a vital role during the crystallization of lanthanum tartrate crystals.

4. Results on growth kinetics show that parabolic kinetics, characteristic of a one-dimensional diffusion-controlled process, is obeyed for a single crystal when the upper reactant concentration is varied.

5. Gel cracking results in channels which quickly drain the upper reactant, leading to an uncontrolled

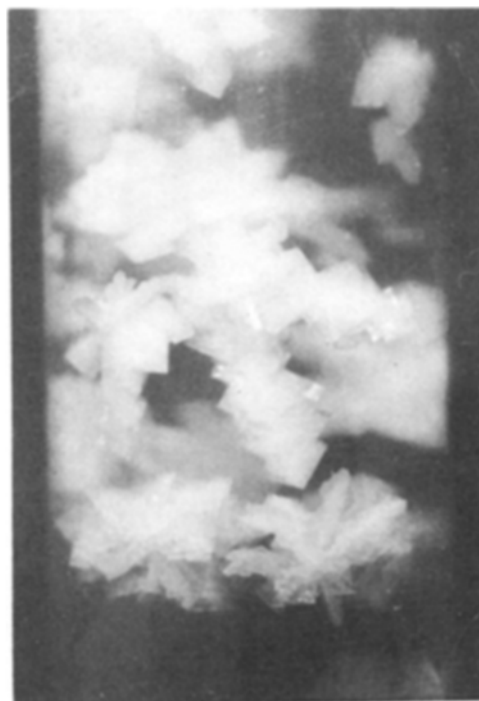


Figure 9 Close-up photograph showing single- as well as multi-arm dendrites growing in the gel growth system.

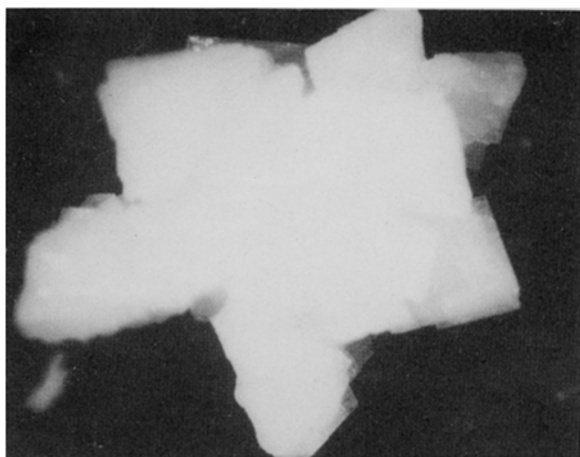


Figure 10 A clump of lanthanum tartrate crystals with multi-arm dendrite growth morphology, as seen under macro-illumination ($\times 8.5$).

number of nuclei and the formation of too many micro-crystallites.

6. The morphology of lanthanum tartrate growing in a silica gel exhibits spherulitic, one-arm and multi-arm dendrites, and single-crystal rectangular platelet growth. The dendritic arms are composed of intergrown platelets of rectangular crystals.

7. Dendrites and spherulites mostly grow in the precipitate zone, while the single platelets of better quality mostly grow in the clear regions at the bottom of the growing system.

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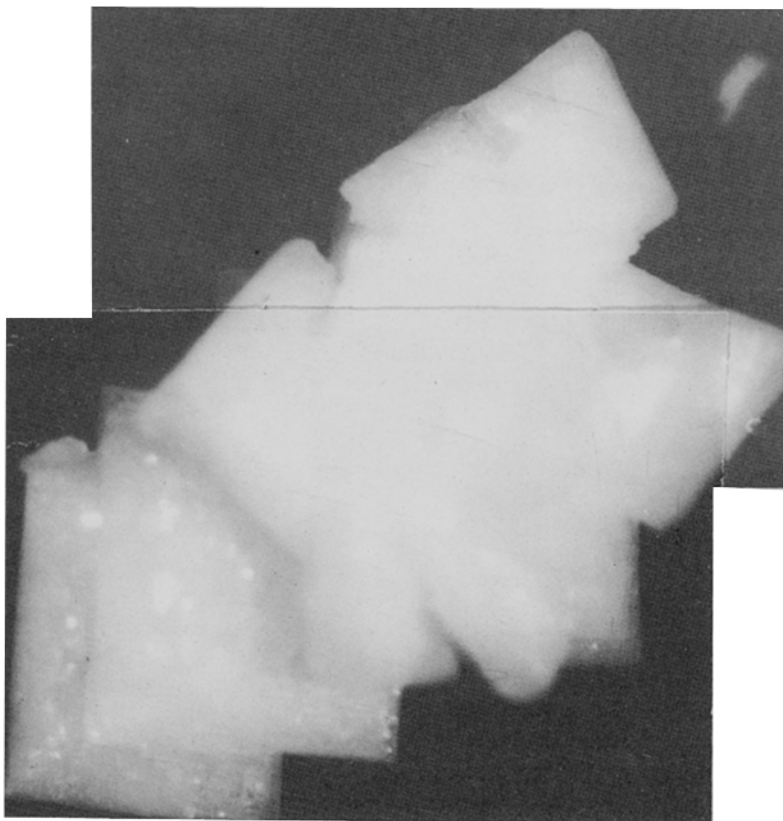


Figure 11 A built-up picture showing dendritic growth with one arm predominant as viewed under a macro-illuminator. The dendritic arm is seen to be composed of intergrown rectangular platelets of lanthanum tartrate crystals ($\times 10$).

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