

# Spherulitic Growth of Neodymium Tartrate Crystals in Silica Gel

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## Abstract:

Neodymium tartrate crystals in the form of spherulites were synthesized in silica gel by using a controlled diffusion system at ambient temperature. The influence of growth parameters such as reactant concentration, gel pH, and gel ageing on the size and nucleation density of the crystals was studied. The mechanisms of crystallization for spherulites are described. Three distinct mechanisms were found to be operative during the crystallization process. Under all conditions the crystals attain spherulitic morphology. This investigation enhances the understanding on spherulitic growth in general and that of neodymium tartrate in particular.

**Keywords:** - Gel growth, Neodymium tartrate, Spherulitic growth.

## I. INTRODUCTION

Crystal growth in gels has made remarkable progress in the recent years. With the pioneering work by Henisch and co-workers [1-2] gel growth research has made rapid strides in the field of crystal growth including growth of materials within the gel. Recently, there have been number of studies on gel-based growth to develop crystals of technological potential. [3-4]. Another factor raising interest in this type of growth is the fact that crystals of various sorts, ionic, organic, and even metallic could be grown at ambient temperature.

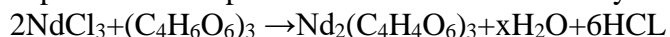
Tartrate crystals are of considerable interest because of their interesting physical properties. Some crystals of this family are ferroelectric [5-7], piezoelectric [8] and quite a few of them have been used for controlling laser emission [9]. Astartrates are sparingly soluble in water and decompose before melting, the gel method is found to be more promising than the high temperature crystal growth methods. Using the gel method many tartrates salts with monovalent cations such as rubidium hydrogen tartrate [10], sodium tartrate [11], and ammonium tartrate [12] have been processed. In addition, tartarate salts with divalent cations such as calcium tartrate [13], cadmium tartrate [14], manganese tartrate [15], zinc tartrate [16] and strontium tartrate [17-18] have been studied. All these salts were studied for their dielectric and thermal properties.

Few tartrate salts with trivalent cations such as rare-earth tartrates ( $R_2(C_2H_4O_6)_3 \cdot xH_2O$  where  $R = La, Ce, Nd, \dots$  elements of lanthanide series) such as lanthanum tartrate [19], holmium tartrate [20], ytterbium tartrate [21] have been studied in the literature. It is pertinent to point out here that so far scanty work has been reported on gel grown rare-earth tartrates (elements of lanthanide series). For a long time now rare-earth compounds have been recognized for their magnetic and luminescent properties. Spherulites are the polycrystalline aggregates. Gel growth leads to spherulitic crystallization in number of cases [22-26], because of which this technique of growth offers means of understanding spherulitic crystallization. In addition, to being a technologically important technique, the problems posed by crystallization leading to spherulitic morphology are intellectually exciting. Recent studies have indicated that rare-earth (Nd, Dy, Di and Gd) tartrates have a tendency to grow in the form of spherulitic crystals containing water of crystallization [27]. The purpose of this paper is to report

growth and discuss the influence of various growth parameters on the growth mechanism of crystals of neodymium tartrate insilica gel at ambient temperature.

## II. EXPERIMENTAL

The growth of neodymium tartrate crystals was achieved by using gel encapsulation technique [28]. The crystallization apparatus for the growth of neodymium tartrate crystals consist of borosilicate glass tube of length 20cm and diameter 2.5cm placed vertically on plastic stand. Silica gel was prepared by acidifying pure sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ) of specific gravity 1.06, with tartaric acid of a concentration in accordance with the requirements of a particular pH value. The tartaric acid solution was added slowly to sodium metasilicate solution with continuous stirring to avoid any local ion concentration which would otherwise cause premature local gelling and make the final solution inhomogeneous. Here, tartaric acid acted as a lower reactant. A fixed amount of gel solution with the desired value of pH was then transferred to several test tubes. The test tubes were sealed with cotton to prevent fast evaporation and contamination of the exposed surface of the gel. The solution was then allowed to set. The gel setting time was found to be strongly dependent on pH. High pH value gel takes lower time to set than low pH value. After confirming the gel setting, aqueous solution of neodymium chloride of the required concentration was then poured slowly along the sides of the tube, to avoid breaking of the gel. Neodymium chloride acted as a upper reactant. Slow diffusion of the upper reactants ions ( $\text{Nd}^{+3}$ ) through the narrow pores of the silica gel lead to reaction between these ions and the ions present in the gel as lower reactant. The following reaction is expected to take place in the formation of neodymium tartrate crystals.



## III. RESULTS AND DISCUSSION

### CRYSTAL GROWTH

Using the crystal growth technique described above tiny faint pink colored spherulitic crystals appeared at precipitate column in about two weeks. The size and the number of crystals increased in few days. Spherulitic crystals growth process took about one month to complete. Series of experiments were performed to obtain the optimum growth conditions for neodymium tartrate crystals. Good quality crystals were obtained only under the following optimum conditions: gel pH of 4.2, gel age of 72h, gel concentration of 1M, and growth temperature of 30-40°C. The best conditions derived here for the growth of neodymium tartrate crystals are based on five experiments conducted on each set of variable parameters. Harvested crystals were removed after 30days. The density of the gel also plays an important role in the growth of the crystals. Below 1.05 gcm<sup>-1</sup>, the medium is soft and above 1.06 gcm<sup>-1</sup>, the gel becomes denser and shows concoidal fracture surface similar to glass. Here, gel density 1.05g cm<sup>-1</sup> was used since this gives the best results. For sodium metasilicate having density 1.05g cm<sup>-1</sup>, the time needed to set the gel properly was found to be one to two days.

### MECHANISM OF CRYSTALLIZATION

Table 1 give the summary of the experiments and the results on size, morphology and nucleation density of the crystals. The results show that under all conditions, the crystals attain spherulitic morphology. It is convenient to discuss the mode of crystallization on the basis of three zones, where distinct mechanisms of crystallization become operative. The first zone is the immediate vicinity of gel-reactant interface. In this zone, on pouring neodymium chloride solution on the top of the gel impregnated with tartaric acid, there is a spontaneous formation of the crust as a result of an instant reaction between the upper and lower reactants. The crust is observed to be a mass of poor quality micro-crystallites. The gel has little part to play, in far diffusions of ions.

The second operative mechanism effective is the crystallization of neodymium tartrate crystals out of precipitate. The precipitate formation, at the gel-reactant interface, starts after 15 to 30 minute depending on gel ageing, on pouring the upper reactant solution. After attaining some thickness, the precipitate begins to advance into gel. Both the upper, as well as lower, fronts of precipitate advance into the gel, but the rate of advancement of the lower front of the precipitate is relatively faster, compared to that of the upper front. Consequently a precipitate column is formed. The advancement of the precipitate continues until the maximum size is reached, which takes about 14 days. At this stage, further advancement of the precipitate

into the gel stops. Usually the precipitate zone is found to be positioned almost in the middle of the gel column.

Table 2 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 keeping the volume of upper reactant and volume gel constant. Figure 1(a) shows the precipitate column after it has ceased to move into the gel. The pattern of advancement of the precipitate is found to be same for all concentrations. However, the total length of the precipitate column depends upon the volume of gel and upper reactant also. The total length of precipitate column is found to be greater for higher volumes of gel and upper reactant.

The precipitate phenomenon finds an explanation on the basis of adsorption properties and its dependence on pH of the gel [29]. This type of phenomenon has been reported by Abdulkhadar and Ittyachen [30] for barium and lead tartrate crystals and by Kotru et al. [31] for rare-earth tartrates and the same explanation is valid in this case too. Silica gel is a polymerized form of silicic acid. Because of high rate of reaction of the reactants, the product of the reaction, neodymium tartrate has no time for regular growth into crystals. As a result of this they are precipitated into colloidal conglomeration. The colloidal particles become adsorbed by the gel, resulting in a column of pink precipitate. As the reaction proceeds, i.e. as neodymium chloride diffuses further into the gel, more and more acid is liberated.

**Table 1 Details of the experiments for the growth of neodymium tartrate**

Experiment	Constant parameters	Changing parameters	Results
1. Variation of gel pH	Upper reactant (neodymium chloride) concentration: 0.75M Lower reactant (tartaric acid) concentration: 1M Gel density: $1.05\text{gcm}^{-3}$ Gel ageing: 72hrs.	Gel pH 4.0 4.2 4.4 4.6 4.8	Morphology: Spherulitic, Max. size of spherulite 6mm diam. at pH 4.2, Nucleation density max. at pH 4, min at pH 5
2. Variation of upper reactant (neodymium chloride) concentration	Lower reactant (tartaric acid) concentration: 1M pH of gel: 4.2 Gel density: $1.05\text{gcm}^{-3}$ Gel ageing: 72hrs.	Upper reactant (neodymium chloride) concentration 0.25M 0.50M 0.75M 1.00M	Morphology: Normal spherulites in all cases, Max. size of normal spherulite: 4mm, Nucleation density: min. at 0.5M conc. of and max at 1M conc. of upper reactant, Below 0.25M con., no nucleation observed.
3. Variation of gel ageing	Upper reactant (neodymium chloride) concentration: 0.75M Lower reactant (tartaric acid) concentration: 1M Gel density: $1.05\text{gcm}^{-3}$ pH of gel: 4.2	Gel ageing 24hrs 36hrs 48hrs 60hrs 72hrs	Morphology: Spherulitic, Crust formation reduces with increase in ageing, Nucleation density, max. at 24h, min. at 72h.
4. Variation of lower reactant (tartaric acid) concentration	Upper reactant (neodymium chloride) concentration: 0.75M pH of gel: 4.2 Gel density: $1.05\text{gcm}^{-3}$	Lower reactant (tartaric acid) concentration 0.25M	Morphology: Spherulites in all cases, Max. size of normal spherulite: 5mm, Nucleation

	Gel ageing: 72hrs.	0.50M 0.75M 1.00M	density: min. at 0.5M and max at 1M conc. of lower reactant, Below 0.25M con., gel does not set.
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With the liberation of the acid, the effective value of pH decreases around the reaction site and force of adsorption decreases with decrease in pH.

Two types of adsorption are considered : (i) adsorption of the colloidal particle by the gel, (ii) adsorption among the colloidal particles. When the top reactant (neodymium chloride) diffuses into the gel, the precipitate formed at the gel-solution interface gradually attains thickness and the material in this band being colloidal particles of neodymium tartrate. When a certain amount of nutrients has reacted, the acid liberated would reduce the force of type (i) to a minimum, hence the colloidal particles move as a band downwards where pH of the gel and consequent force of adsorption is large. In this way the thickness of the precipitate continues to increase as the colloidal particles of neodymium 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 minimum and rendering the colloidal particles free. At this stage, the colloidal particles diffuse into the growth sites and the crystals start to grow. Figures 1(b)-(d) show three tubes of growing neodymium tartrate crystals. It is noticed that within the precipitate zone the formation of crystals takes place in the form of spheres. This can be attributed to the presence of too many nuclei and the variation of the effective value of the pH within the precipitate zone. It was observed that no crystal growth takes place outside the precipitate zone in case of neodymium tartrate. Harvested crystals of neodymium tartrate are shown in Figure 2.

**Table 2 Rate of advancement of colloidal precipitate in the gel column.**

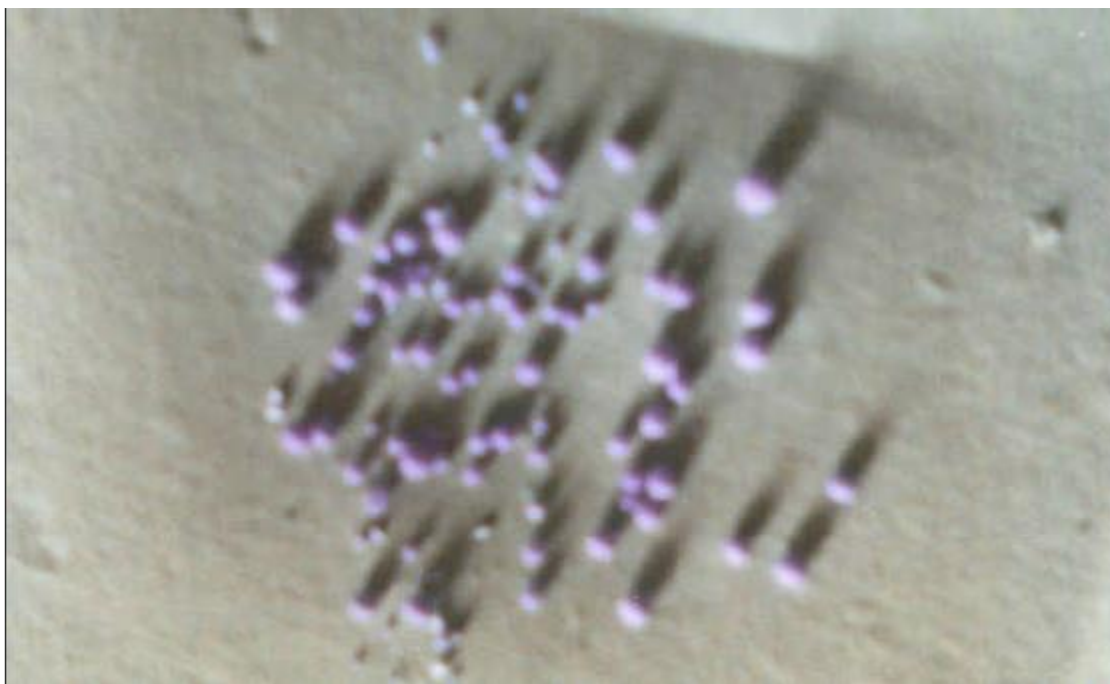
Tube No.	Conc. of upper reactant (M)	Period of advancement of precipitate (h)	Reading of precipitate boundaries from gel-reactant interface		Observed length of gel column (cm)	Rate of advancement	
			Upper boundary (cm)	Lower boundary (cm)		Upper boundary $\times 10^{-3}$ cm/h	Lower boundary $\times 10^{-3}$ cm/h
1	0.25	360	1.2	2.2	1.0	3.33	6.11
2	0.50	360	1.3	2.8	1.5	3.61	7.77
3	0.75	360	1.3	3.8	2.5	3.61	10.5
4	1.00	360	1.4	4.5	3.1	3.88	12.5

The second operative mechanism of crystallization in precipitate zone has distinct features. Soon after attaining stability in size and position over a week, nucleation of crystals starts. Each nucleation center is found to be associated with halo, i.e. a spherical region in which gel is depleted of colloidal particles. The colloidal particles surrounding the nucleation center tend to migrate radially towards it from all directions, resulting in the increase in size of the halo. The halo is many times bigger than the size of the crystal and filled with a clear solution resulting in transparency within it. The halo grows as the crystal grows. In case where there are more than one nucleation centers in close proximity, halos in course of time merge into each other. The process continues until the whole precipitate in the column is dissolved, resulting in a clear zone with number of crystals. In case of neodymium tartrate it was observed that rate of depleting the

colloidal precipitate increases as size of the crystals increases. In third zone, where there is no precipitate formation, crystallization also takes place. This zone is below the precipitate zone. The crystallization is very rare in this zone because of lower concentration gradient. In this region crystals growing are more perfect spherulites.



**Figure 1**(a) Formation of halo in the precipitate; (b) growth conditions: Gel pH = 4.2, Conc. of upper reactant = 1M; (c) growth conditions: Gel pH = 4.2, Conc. of upper reactant = 0.75M; (d) growth conditions: Gel pH = 4.2, Conc. of upper reactant = 0.5M



**Figure 2** Spherulitic crystals of neodymium tartrate.

## CONCLUSION

From the experiments on the growth of neodymium tartrate crystals in the system  $\text{NdCl}_3\text{-Na}_2\text{SiO}_3\text{-C}_4\text{H}_6\text{O}_6$ , the following conclusions may be drawn:

1. The growth of neodymium tartrate crystals is accomplished by allowing diffusion of neodymium chloride through silica gel impregnated with tartaric acid in a single-gel-single tube system.
2. The crystals exhibit spherulitic morphology even under varied conditions of growth. Maximum size of the spherulite under optimum conditions was 6mm in diameter.
3. The instant reaction between the two reactants at the gel reactant interface leads to the formation of a crust whose building blocks are tiny crystals. Improved ageing reduces the crust formation.
4. Three distinct mechanisms play a part in the crystallization of neodymium tartrate crystals: 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. This third mechanism is dominant in case of neodymium tartrate crystals.

5. The adsorption property of a gel plays an important role during the crystallization of neodymium tartrate crystals.
6. Spherulitic formation may arise due to agglomeration of tiny crystallites orienting and accommodating themselves in spherical shape. The same process may continue till the cessation of crystal growth process. Thus spherulitic crystals of neodymium tartrate are polycrystalline in nature.

## ACKNOWLEDGEMENT

Author is thankful to The Principal, Head of the Physics Department, Pratap College, Amalner and Principal, J.E.S.S Arts, Science and Commerce College, Nandurbar for necessary facilities provided to carry out the present work.

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