JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Growth of Cerium Tartrate Crystals by Gel Method: A Study on Growth Parameters and Morphology

H.M. Patil

Associate Professor
Department of Physics
JES's Arts, Science and Commerce College, Nandurbar, (M.S), 425412, India

Abstract: Cerium Tartrate crystals have been successfully grown using the gel method, a novel technique for crystal growth. The crystals were grown in a silica gel medium, and their morphology, structure investigated. Effect of nucleation controlling parameters such as Effect of pH of gel, Gel density , ageing of the gel, Effect of concentration of feed solutions were studied. The results show that the gel method yields Spherulitic cerium tartrate crystals with well-defined morphology. The gel method offers a controlled and slow growth rate, allowing for the formation of Spherulitic crystals. The study demonstrates the potential of the gel method for growing tartrate crystals of lanthanide series elements.

Keywords:- Lanthanide series elements, tartrate crystals, gel method, crystal growth, morphology, structure, gel pH, aging of gel.

1. INTRODUCTION

Cerium is unique among other rare earth metals with only a single electron in the 4f shell when it is in ionic state. Its optical, luminescent and magnetic properties are studied widely. Cerium (Ce3+) is used as a co-dopant in certain photo refractive crystals like LiNbO3, KNbO3 and SrxBa1-xNb2O6 [1] and laser crystals like Y3Al5O12:Nd and YAlO3 [2]. Several compounds containing cerium are under study for their ferromagnetic, antiferromagnetic and superconducting properties. Optical and luminescent properties of laser scintillator crystals like YAG and YAP doped with Ce3+ ions are studied [3]. Studies on cerium oxalate crystals grown in hydro-silica gel have been reported [4]. Growth and characterization of several oxalates and mixed rare earth oxalates in silica gel also have been reported [5-7]. No report has been noticed on the study of cerium tartrate. Hence growth of these crystals is attempted. Cerium tartrate can be grown by gel technique since it has very low solubility in water. Growth and characterization of several tartrates and mixed rare earth tartrates in silica gel have already been reported. Grown crystals can be furtther characterized by different methods. Effect of nucleation controlling parameters such as Effect of pH of gel, Gel density , ageing of the gel, Effect of concentration of feed solutions were studied is attempted in the present work.

2. EXPERIMENTAL PROCEDURE AND OBSERVATIONS

The growth of cerium tartrate crystals were accomplished by the controlled diffusion of Ce^{+3} ions through the silica gel impregnated with tartaric acid. To accomplish the growth of cerium tartrate crystals the gel solution is prepared from sodium metasilicate [8-9]. All experiments were carried out by single tube diffusion method. The tubes employed were borosilicate glass tubes of 2.5cm diameter and 20cm long. The experiments were carried out at ambient temperature. Silica gel was prepared by adding a solution of sodium metasilicate of specific gravity 1.05gm/cm^3 to tartaric acid (0.25M-1.0M), drop by drop with continuous stirring to avoid excessive local ion concentration, which may cause premature gelling and make the final solution inhomogeneous. The pH of the gel was adjusted between a value of 3.4 and 4.8.The solution with the desired value of pH was then transferred to several glass tubes. Once gelled, an aqueous solution of cerium chloride (0.25M-1.5M) was carefully poured with the help of a pipette over the set gel, in order to avoid any gel breakage. The mouth of the test-tube is then covered with cotton plug to avoid the inclusions of impurities.

The expected chemical reaction employed for the growth of cerium tartrate crystals is

$$2CeCl_3 .7H_2O+ 3(C_4H_6O_6) \rightarrow Ce_2 (C_4H_4O_6)_3 \, xH_2O+ 6HCl$$

The slow diffusion of the Ce+3 ions into the gel and their subsequent reaction with the tartrate ions results in the formation of the expected crystals. A typical experimental setup is shown in Fig. 1

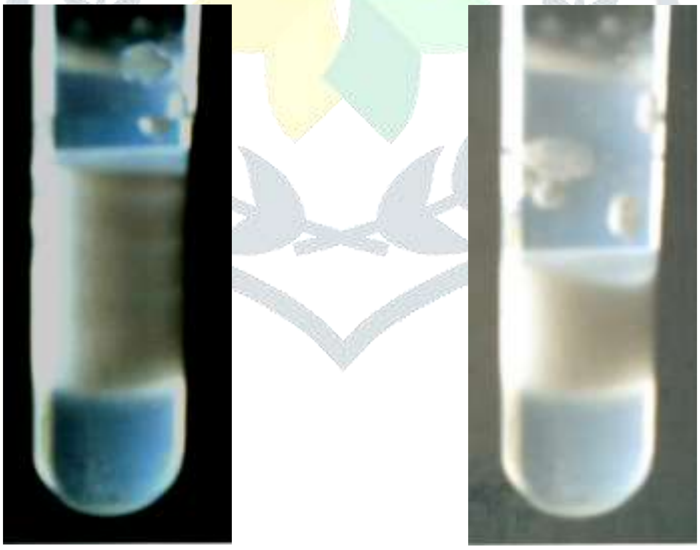
In order to find out the best condition for the growth of perfect crystals, a number of experiments were conducted by changing the various parameters like pH of gel, concentration of reactants, gel ageing and density. The optimum conditions for the growth of pure cerium tartrate crystals deduced are given in Table 1.

Table 1 Optimum conditions for the growth of lanthanum tartrate crystals

Growth Parameter	Optimum value
Gel pH	4.2
Gel density	1.05gm/cm^3
Gel ageing	72hr
Concentration of lower reactant (Tartaric acid)	1M
Concentration of upper reactant (Cerium chloride)	0.5M
Temperature	27-30oC

(b)

Figure 1 Typical experimental setup in the laboratory



(a) (b)

Figure 2 Photograph of spherulitic crystal formation in gel

3. EFFECT OF NUCLEATION CONTROLLING PARAMETERS

3.1 Effect of pH of gel: The impact of pH on the growth of cerium tartrate crystals has been studied by varying the pH of the medium from 3.5 to 6 by increasing the level of the tartaric acid in the gel medium. All the other variants are kept constant for this experiment. The Maximum thickness of precipitation with pH is shown in Fig. 3. At lower pH values, grater thickness of precipitate zone was observed. Crystals grow at all pH but their size and quality have been changed considerably with changes in pH. For gel of pH 6 or less crystal growth is observed at the gel solution interface region. As tartaric acid being the acidifying agent, a low pH in the present context means a high level of the anionic concentration. Thus the concentration conditions are easily attained near the interface when the pH is lowered and this in turn generates crystals at this place. By increasing the pH, the gel gets hardened and it reduces the rate of diffusion of the ions. The decrease in the density of population of the crystals with pH may be due to this effect. The optimum value of pH for the growth of these crystals is 4.2 at which the crystals obtained are of perfect quality and the size averaged 3mm.

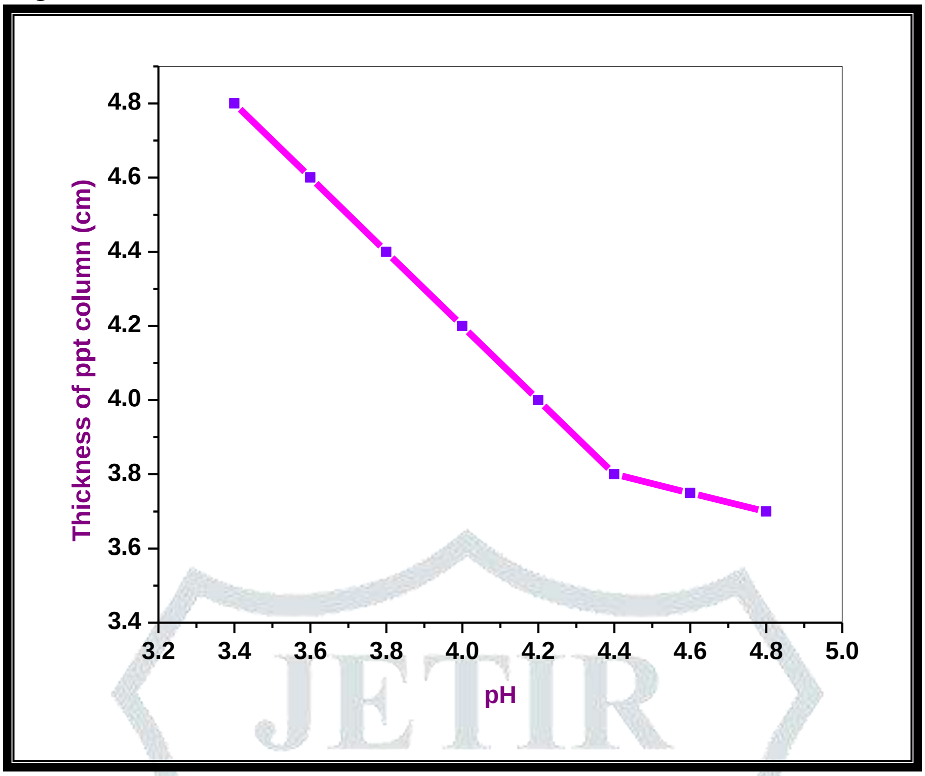


Figure 3 Maximum thickness of ppt. with pH

3.2 Gel density and ageing of the gel: Changes due to gel density and ageing of the medium are studied during the growth of these crystals. Twinned crystals are formed when the density of the gel is increased. As the hardening of the gel medium may impose constraints on the growing face of the crystal, this will affect the quality of the crystal. Gel ageing also hardens the medium but this is due to the dehydration. Tubes containing gels of age 20 days or more do not exhibit any crystallites up to 2cm below the gel solution interface. The top surface of the gel has been dried and as a result the follicles which contain anions have been withered off. The down diffusants have to travel more to achieve the minimum concentration condition in order to establish the growth. Sometime it may be due to a non-uniform hardening of the gel column. The top surface of the gel may have hardened more than its lower part. The diffusion of the anions is thus retarded.

3.3 Effect of concentration of feed solutions: After pouring the feed solution a thin white precipitate layer of small thickness is found to form on the gel solution interface. Thickness of the precipitation is increased with the concentration of the upper reactant while other parameters are kept constant. This is because of the greater concentration of the ions at the gel solution interface and high rate of reaction. Variation of thickness of the precipitation zone after it is ceased to advance in to the gel column is shown in Fig.4.

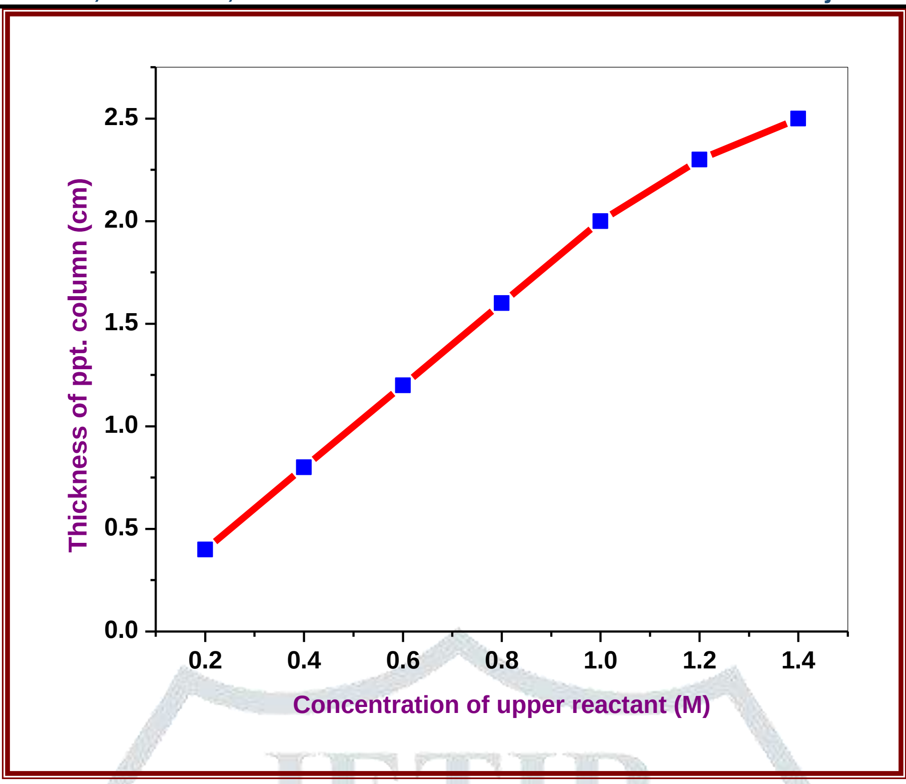


Figure 4. Maximum thickness of ppt. with concentration of upper reactant

It was also observed that displacement of precipitation front increased directly with the concentration of the outer electrolyte and inversely with that of the inner electrolyte. The density of the colloidal precipitate which can be varied by varying the concentration of the outer electrolyte was higher for a higher concentration of the outer electrolyte. The density decreased at a higher depth in the gel column. The partial dissolution began from the bottom of the precipitate. This dissolution led to crystallization. Crystals formed in the region of denser precipitate was of the clustered type. Single crystals were formed in the regions of lesser density of the precipitate and the size of the crystals was small. When the density of the colloidal precipitate was small, dissolution was easily possible and the rate of consumption of nutrient over a given length of the gel column was less.

Fig. 5 and Fig. 6 show the effect of variation of the outer electrolyte on precipitation front and partial dissolution region respectively.

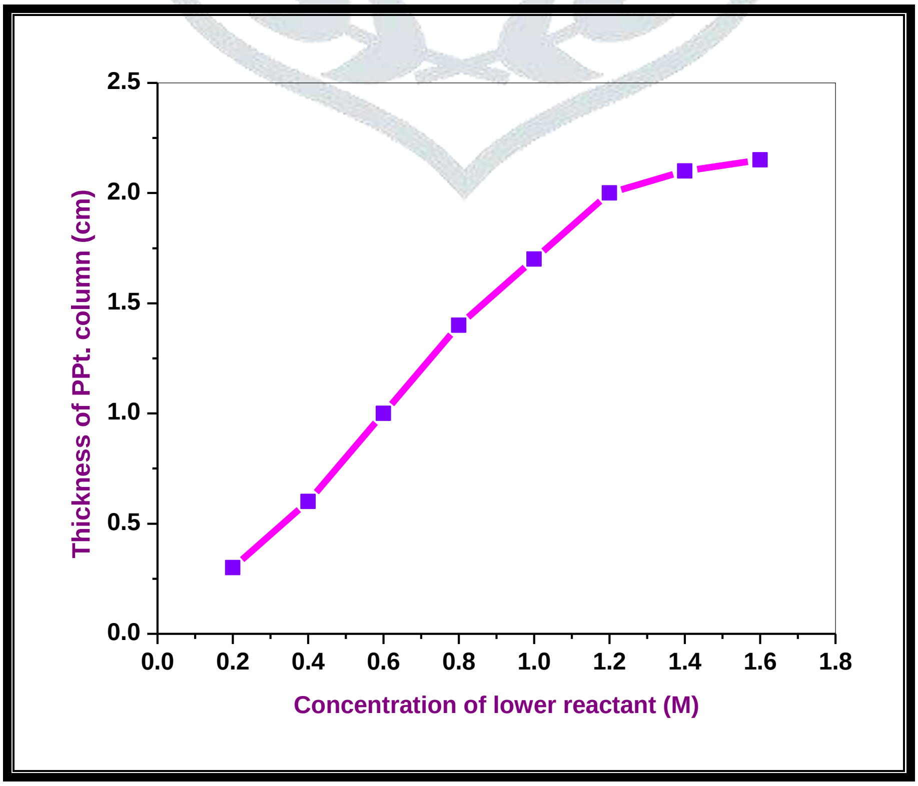


Figure 5 Maximum thickness of ppt. with concentration of lower reactant

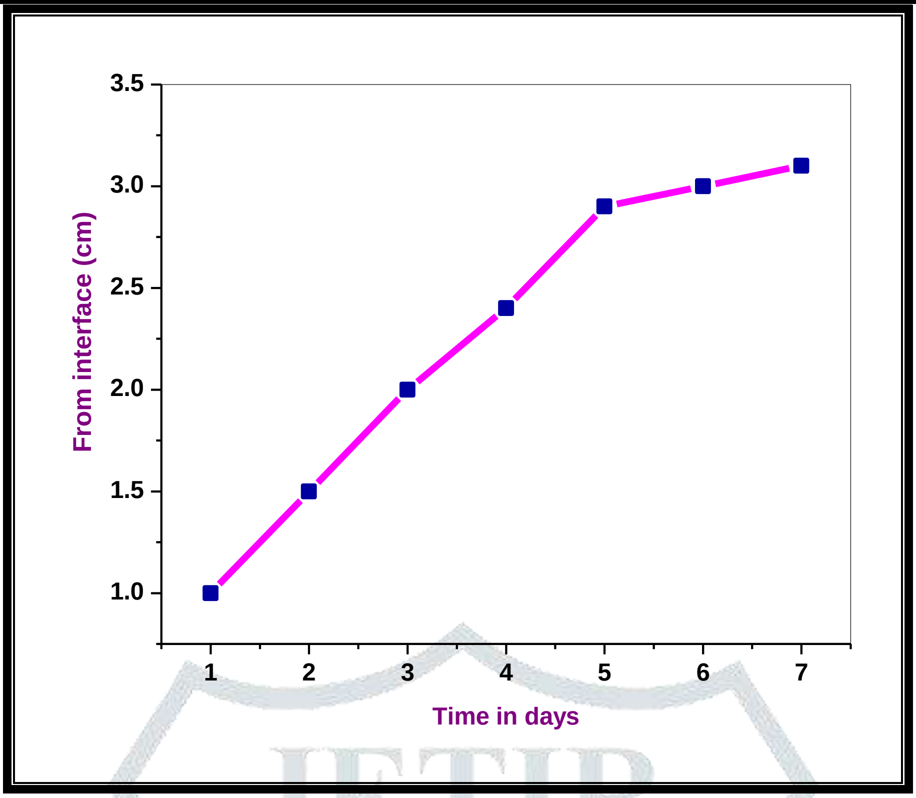


Figure 6 Effect of variation of upper reactant on advancement of precipitation front

4. Results and Discussion on Crystal Growth of Cerium Tartrate Crystals

Table 2 gives a detailed summary of the experiments performed and results obtained thereof on the morphology, nucleation density and size of cerium tartrate crystals grown in silica gel. The results show that crystals of cerium tartrate grow at a gel of pH 3.6, 3.8, 4.0 and 4.2, 4.4. For all pH values crystals attain spherulitic morphology.

As soon as the upper reactant (cerium chloride) is poured over the set gel containing tartarte ions, there is an instantaneous reaction between the cerium and tartrate ions resulting in the spontaneous formation of a precipitate.

It is observed that the strength of precipitation depends profoundly on the gel pH, higher the pH, stronger is the precipitation; other parameters of the growth like upper and lower reactant concentrations, gel age, gel density remaining the same. For gel pH > 3.6, a strong precipitate is observed to form at the gel solution interface. Due to this, the supersaturation available for three dimensional surface nucleation and growth becomes very high which results in the formation of spherulites. However, at lower values of gel pH (<3.6), negligible precipitation occurs at the gel solution interface upon pouring of upper reactant and after a period of 10 days, very small single crystals of cerium tartrate start appearing at different sites near the gel solution interface.

The concentration of the precipitant ions decreases with the decrease in pH [10]. Therefore degree of precipitation depends strongly on pH of the medium. Secondly, in a low pH medium the solubility of cerium tartrate gets raised with the result that the local concentration product $[Ce^{3+}][(C_4H_4O_6)^{2-}]$ becomes less than the solubility product Ksp [11]. Otherwise, if local concentration product is greater than Ksp a strong precipitation occurs at the interface, which often leads to the formation of spherulites as well as amorphous precipitate.

Due to this, the value of supersaturation developed at different sites inside the gel changes and becomes as low as may be appropriate for the growth of single crystals. However, it was also observed that at low pH values the nucleation density become very high which puts a limit to the size of crystals.

It was further observed that even few crystals grew near the bottom of some tubes, which were initially set at gel pH 4.8 and were kept for about three months. It could be because of the fact that as the reaction proceeds for the formation of stable product (cerium tartrate); there is release of HCl as a by-product, which further reduces the pH of the gel medium. After such a long period, the pH of the medium was reduced to a much lower value of 2.5. This observation was confirmed by measuring the pH of the gel medium at the time of gelling and at the time of taking out the crystals from the gel.

Fig.2 shows some spherulitic crystals growing in a crystallizer containing gel of initial pH value 4.2 Optical photographs of some as grown spherulitic cerium tartrate crystals are shown in Fig 7.

Table 2 Summary of the experiments on the growth of cerium tartrate crystals in silica gel.

Experiment	Variable parameter	Constant parameters	Observations
Effect of gel pH	Gel pH: 3.6 3.8 4.0 4.2 4.4 4.6	Conc. of upper reactant: 0.75M Con. of lower reactant: 1M Gel density: $1.05 gm/cm^3$ Gel age: 72hrs.	1. Normal and coalesced spherulites for all pH values. 2. Maximum size of spherulite at pH 4 was 6mm diameter. 3. Nucleation density: Maximum at pH < 3.8 and Minimum at pH>4. 4. Strength of precipitate minimum for pH < 3.8 and maximum for pH>4
Effect of concentration of lower reactant (Tartaric acid)	Concentration(M) of lower reactant: 0.25 0.50 0.75 1.00 1.25	pH: 4.2 Conc. of upper reactant: 0.75M Gel density: $1.05 gm/cm^3$ Gel age: 72hrs.	1. Normal spherulites for all cons. <0.75M 2. Coalesced spherulites were observed for cons. > 0.75M 3. Length of precipitate column is minimum for conc. < 0. 75M and maximum for conc. > 1.25M 4. Increase in length of precipitate ceases beyond con. 1.25. 5. Maximum size of spherulites at 1.0M was 5mm.
Effect of concentration of upper reactant (Cerium Chloride)	Concentration(M) of upper reactant: 0.25 0.50 0.75 1.00 1.25	pH: 4.2 Conc. of lower reactant: 1.0M Gel density: $1.05 gm/cm^3$ Gel age: 72hrs.	1. Normal spherulites for all cons. <0.75M 2. Coalesced spherulites were observed for cons. > 0.75M 3. Length of precipitate column is minimum for conc. < 0.75M and maximum for conc. > 1.25M 4. Increase in length of precipitate ceases beyond con. 1.25. 5. Maximum size of spherulites at 0.75M was 5mm.
Effect of gel density	Gel density: (gm/cm3) 1.02 1.04 1.05 1.06	pH: 4.2 Conc. of upper reactant: 0.75M Conc. of lower reactant: 1.0M Gel age:72hrs.	1. Normal spherulites for all selected densities 2. Nucleation density is maximum at density 1.02(gm/cm3) and minimum at 1.06(gm/cm3), higher density gels beyond 1.06 does not proved fruitful. 3. Maximum size of spherulite at density 1.05 was 7mm
Effect of gel age	Gel age: 48hrs. 72hrs. 120hrs. 144hrs.	pH: 4.2 Conc. of upper reactant: 0.75M Conc. of lower reactant: 1.0M Gel density: $1.05 gm/cm^3$	1. Normal and coalesced spherulites for all age values. 2. Nucleation density is maximum at gel age of 48 hrs and minimum at a gel age of 144hrs. 3. Increase in length of precipitate ceases beyond con. 1.25. 4. Maximum size of spherulites at gel age of 72 hrs was 5mm.

5. Morphology of the crystals

Fig.7 shows the optical photograph of as grown crystals outside the crystallization vessel. In most cases the crystals formed near to the interface (greater diffusion region) were clustered, twinned and multiple crystals. Towards the middle of the crystallization region clustering and multiplicity were reduced. At the bottom of crystallization region i.e. at greater depths, where diffusion is controlled, good crystals were formed.

Towards the gel solution interface, along with the crystals, the formation of spherulites also was commonly observed. It was observed that the nucleation took place within the precipitated zone with the creation of a hollow around each nucleation centre. The hollow, a spherical region in the gel column, was depleted of the colloidal particles of the precipitate and the volume of the hollow increased with the increase in the size of the spherulite. The free colloidal particles of the precipitate occupied the hollow region around the active nucleation site, thus condensing into a spherulite crystal, thereby, attaining a smaller volume. The periphery of the hollow formation is the reflection of the condensed matter as shown in Fig. 8.

(a) (b) (c)

Figure 7 Optical photograph of spherulitic crystals of cerium tartrate outside the crystallization vessel

Figure 8 Condensed matter formed within the halo

6. 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 cerium tartrate crystals.
2. The diffusion of Ce^{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 = 1.05gcm^{-3}; gel ageing for 72h; concentration of lower reactant = 1M; Concentration of upper reactant =0.5M.
3. Grown crystals exhibit varied morphology such as spiky spherulites, multi-arm dendrites and rectangular platelets.
4. Crystallization of cerium 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 cerium 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.

ACKNOWLEDGEMENT

The author is much indebted to authorities of Pratap College, Amalner for carrying out the present work. The author is thankful to Dr. Dilip Bhavsar, Pratap College, Amalner for his inspired suggestions.

REFERENCES

1. Shedam, M.R. and Venkateswara Rao, A., Bull. Mater. Sci., 16 (**1993**) 309.
2. Cyriac Joseph, George Varghese and Ittyachen, M.A., Cryst. Res. Technol., 30 (**1995**) 159.
3. Cyriac Joseph, Ittyachen, M.A., and Raju, K.S., Bull. Mater. Sci., 20 (**1997**) 37.
4. Bunn, C.W. and Alcock, T.C., Trans. Faraday Sci., 41 **(1945)** 317.
5. Keller, A., Polym. J. Sci., 17 **(1955)** 291.
6. Bhat, S., Kotru, P.N. and Koul, M.L., Mater. Sci. Engg., B34 **(1995)** 138.
7. Kotru, P.N. and Raina, K.K., J. Mater. Sci. Lett., 5 **(1986)** 760.
8. Henisch, H.K., Dennis, J. and Hanoka, J.I., J. Phys. Chem. Solids, 26 **(1965)** 493.
9. Henisch, H.K., *Crystal Growth in Gells*, Pennsylvania State University Press, University Park, Pennsylvania, **1970**.
10. Alexeyev, V., *Quantitative Analysis*, Mir Publishers, Moscow, **1969** 84.
11. Laudise, R.A., *The Growth of Single Crystals*, Prentice-Hall, Inc. Englewood Cliffs, New Jersy, 272