ISSN : 0974 - 746X Volume 7 Issue 3

Inorganic CHEMISTRY

Trade Science Inc.

An Indian Journal

Full Paper

ICAIJ, 7(3), 2012 [95-98]

Effects of gel parameters on nucleation and growth of $Ni_{1-x}K_xHC_4H_4O_6$ single crystals in silica hydro gel

M.K.Gondalia*, R.N.Patel

Physics Department, Kamani Science College, Amreli-365601, (INDIA)

E-mail: mkg.ksc@gmail.com

Received: 6th March, 2012 ; Accepted: 27th April, 2012

ABSTRACT

The influence of different gel parameters, concentration programme and replenishment programme on nucleation and growth of nickel doped potassium hydrogen tartrate (NPHT) crystals are discussed. The nucleation control can be achieved by varying a variety of gel parameters such as gel density, gel pH, gel ageing and concentration of feed solution. The size of the crystals can be increased by replenishment programme. Increase in the concentration of feed solution, nucleation density increases. By concentration programme, the size of NPHT crystals improved but transparency decreased. Gel ageing reduces the growth rate of crystals.

KEYWORDS

NPHT;
Nucleation density;
Gel ageing;
Replenishment programme.

INTRODUCTION

The nucleation control is important in any gel system. Gel medium prevents turbulence, acts as a catalyst, and permits the electrolytes to diffuse at a desired controlled rate and yields good quality crystals[1]. The gel is to stabilize concentration gradients in the neighborhood of growing crystals by suppression of convection currents[2]. It is envisaged that the potential nuclei are physically enclosed in gel cells of varying sizes and varying degrees of concentrations with neighboring cells. Thus many nuclei would be rendered ineffective if they are located in cells either too small or too isolated to support visible growth. Gel cell size is influenced by gel density, gel age[3], pH of gel[4], temperature[5], etc. Hence nucleation control is achieved to some extent by varying these parameters.

Nickel doped potassium hydrogen tartrate (NPHT) crystals have been grown previously using silica hydro gel. This paper describe the effect of gel parameters, concentration of feed solution and replenishment programme on nucleation and growth of NPHT single crystals using silica hydro gel.

EXPERIMENTAL PROCEDURE

The crystallization apparatus used in the present study are the usual test tube, of length 15 cm and diameter 2.5 cm. A stock solution from 0.2 M sodium meta silicate (Loba grade) with density 1.03 g cm^{-3} was prepared. Aqueous nickel chloride (Analar BDH grade) solution with 0.05 to 1.5 M concentration and potassium chloride (Analar BDH grade) solution with 0.05 to 1.5 M were also prepared. The different pH values of gel solutions used are 3.5, 4.0, 4.5 and 5.0. In the test tube, pH of the gel solution was controlled by tartaric acid and with addition of nickel chloride and potassium chloride solutions.

The gel is formed with tartaric acid and the top solutions were nickel chloride and potassium chloride.

In all the cases, the following reactions are expected.

$$(1\text{-}x)\,NiCl_2 + x\,KCl + C_4H_6O_6 \rightarrow Ni_{1-x}K_xH\,C_4H_4O_6 + HCl$$

The details of crystal growth study are presented elsewhere. The growth experiments are repeated by varying pH of gel, ageing of gel, gel density, replacing the feed solution as well as the concentration of the reactants in order to determine the best experimental conditions for the growth of large and well formed crystals as shown in figure 1.

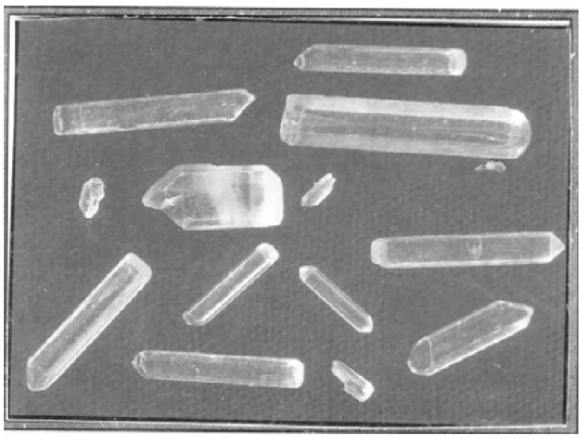

Figure 1 : Nickel doped potassium hydrogen tartrae single crystals

RESULTS AND DISCUSSION

Six different effects on NPHT crystals were observed under various conditions. Well defined regular as well as irregular shaped needle type transparent crystals up to 2.9 cm in length are observed.

Effect of concentration of feed solution

To investigate the effect of concentration of feed solution, the gel of certain pH and density are prepared. The solution of $NiCl_2 6\,H_2O$ and KCl of 0.25 M to 1.0 M are poured over the set gels. The variation of the nucleation density with the concentration of feed solution is obtained as shown in figure 2. It indicates that the nucleation density increases at higher concentration of feed solutions because of the enhanced availability of nickel and potassium ions. It is observed that the higher concentration of feed solution give rise to long needle shaped crystals. This may be due to an increase in the super saturation at higher concentration of feed solution.

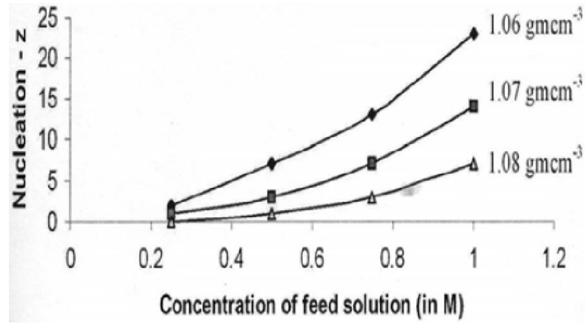

Figure 2 : The variation of nucleation density with concentration of feed solution

Effect of gel density

By mixing sodium metasilicate solution of specific gravity 1.06, 1.07, 1.08 and 1.09 g cm^{-3} with 1.5 M tartaric acid, gels of various densities are prepared. The pH of gel kept at 4.0. Figure 3 shows a plot of nucleation density versus gel density. A greater gel density implies a smaller pore size and poor communication among the pores and thereby nucleation density decreases. The increase in gel density also causes the contamination of the silica gel with NPHT crystals and therefore affects their quality and shape. A gel density of 1.04 g cm^{-3} gives good transparent NPHT crystals. Density of gel more than 1.06 g cm^{-3} gives big crystals but they are less transparent. It may be noted that a gel density of 1.06 g cm-3 is the optimum value for the growth of fairly transparent and big well defined single crystals of NPHT.

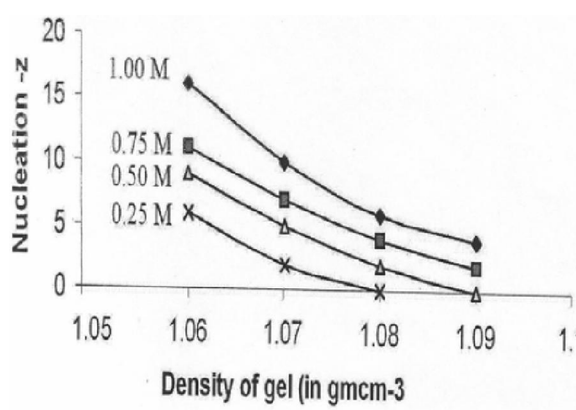

Figure 3 : The variation of nucleation density with gel density

Effect of pH of gel

The pH values of gel are varied from 2.0 to 10.0

by the addition of tartaric acid of various concentrations. TABLE 1 shows the proportion of tartaric acid (V_T) and sodium metasilicate (V_M) to secure the desired pH of gel solution. Figure 4 illustrate the variation of nucleation density with the pH of gel. The gel transparency decreases with increase in gel pH. The NPHT crystals growing at higher pH values are opaque and poorly defined. This is due to contamination of crystals by silica gel, because as the pH increases, the box like structures of gel changes to a loosely bound platelet structure without cross linkages and the cellular nature become less distinct. It is found that the nucleation density decreases with increasing pH, which may be due to improper formation of the cells at higher gel pH.

TABLE 1

Tartaric Acid 1.5 M (V_T ml)	Sodium meta silicate 1.06 g cm^{-3} (V_M ml)	V_M/V_T	pH of gel solution
53	100	1.88	2
35	100	2.86	3
19	100	5.26	4
15	100	6.66	5
12	100	8.33	6
8	100	12.5	7
6	100	16.66	8
4	100	25.00	9
2	100	50.00	10

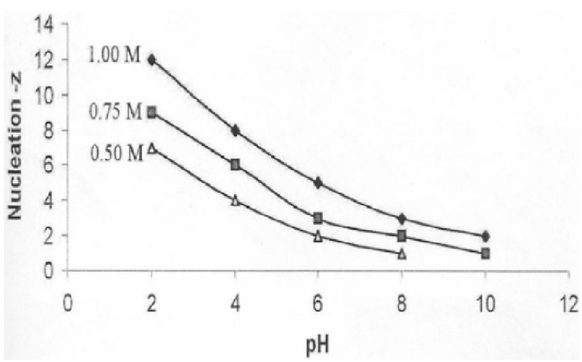

Figure 4 : The variation of nucleation density with pH of the gel

Effect of gel ageing

Gels are allowed to age for various periods before adding the feed solutions ($NiCl_2 6 H_2O$ and KCl). Figure 5 shows a plot of ageing of gels versus nucleation density. Gel ageing reduces the cell size and consequently the rate of diffusion of nickel and potassium ions into the gel. Typical NPHT crystals are grown in gels for the age of three different periods. It is observed that longer a gel set period, more amount of water evaporates out of the gel. The evaporation of water causes an increase in gel density which in turn decreases the diffusivity of nickel and potassium ions in the gel, thereby decreases number of nucleation sites.

Evaporation of eater causes not only the lack of ionic carriers in the channel of the gel framework, but also discontinuities in the channel due to shrinkage of gel. Both these effects would adversely affect the diffusion of nickel and potassium ions and hence the number of nucleation centers.

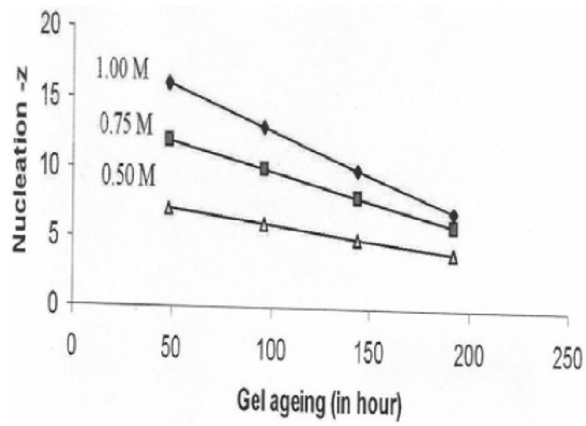

Figure 5 : The variation of nucleation density with the ageing of gel

Replenishment programme

The size of the grown NPHT crystals can be considerably increased and the nucleation centers can be controlled by continued supply of reagent and by removing the waste product. This can be achieved by periodically replacing the feed solutions of same concentration. The 20 ml solution of 0.5 M nickel chloride and 0.5 M potassium chloride is placed over the set gel, and after 3 days this solution was replaced by the fresh 20 ml of the same solution. This process is continued for one month.

The replaced solution will be able to maintain a dynamic equilibrium and a flux of solute owing to diffusion at the growing NPHT crystals. Thus there will be a constant new diffusion gradient throughout the crystal growth. Thus the probability of formation new nuclei is reduced and size of growing NPHT crystals becomes larger. By this method transparent and large NPHT crystals are grown.

Concentration programme

In this procedure, 20 ml of 0.25 M $NiCl_2 6 H_2O$ + KCl solution is placed over the set gel. The strength of this feed solution is increased at the rate of 0.25 M per every two day by removing the older one. Initially very poor nucleation was observed but at 0.5 M concentration, nucleation becomes maximum. After that no more new nucleation but size of crystals increases, rather above 0.5 M concentration of feed solution, the crystals becomes successively opaque and then hollow. This resulted in a few nucleation centers, which acted as sinks and used in the establishment of a radial diffusion pattern that substantially reduced the reagent concentration in the neighboring locations and hence the formation of additional nuclei is inhibited.

ACKNOWLEDGEMENT

Author is thankful to Prof. K D Patel, Physics Department, Sardar Vallabhbhai Patel University, Vallabhvidhyanagar and Dr. V. N. Patolia, Chemistry Department, Kamani Science College, Amreli for his valuable support to prepare this paper.

REFERENCES

[1] S.N.Patil, A.V.Rao; Cryst.Res.Technol., **26**, 841 **(1991)**.

[2] H.K.Henisch; Crystals in Gels and Liesengang Rings, the Pennsylvania State University, Cambridge University Press **(1988)**.

[3] P.N.Kotru, N.K.Gupta, K.K.Raina; Cryst.Res.and Tech., **21**, 15 **(1986)**.

[4] A.R.Patel, A.V.Rao; J.Cryst.Growth, **43**, 351 **(1983)**.

[5] K.Nassu, A.S.Copper, J.Shiever, B.E.Prescott; J.Solid State Communi., **8**, 263 **(1973)**.