ISSN : 0974 - 746X Volume 7 Issue 2

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 7(2), 2012 [61-64]

Growth features of nickel doped potassium hydrogen tartrate single crystals in silica hydro gel

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Received: 21st January, 2012 ; Accepted: 15th March, 2012

ABSTRACT

The growth of nickel potassium tartrate in silica hydro gel at ambient temperature has been successfully carried out. The effect of various parameters: like gel pH, gel ageing and concentration of reactants on the growth of these crystals have been studied. The grown crystals are characterized by chemical analysis, X-ray powder diffractometry and infrared spectrometry. The results of these observations have been described and discussed.

KEYWORDS

NPHT;
Nucleation density;
Infrared absorption spectra;
X-ray power diffraction.

INTRODUCTION

Growth of crystal in gel medium paid much attention by research workers after the fundamental work by H. K. Henisch. It has been reported[1-4] that a variety of crystals suitable for research and technology can be grown in silica hydro gel. This method is useful for the growth of compounds, which are insoluble or sparingly soluble in water and also which cannot be conveniently grown from melt or vapour phase. The gel medium prevents turbulence and remaining chemically inert, provides a three dimensional structure which permits the reagents to diffuse at a desirable controlled rate.

Most tartrate crystals are insoluble in water and decompose before melting. Hence, single crystals of compounds cannot be grown by either slow evaporation or melt techniques but they can be suitably grown by gel method. Mixed crystal growths employing the gel technique are very scarily tried[5,6] and the field is in an early stage of development with many opportunities to create new species. Some tartrate crystals are well known for its ferroelectric properties in pure[7] as well as doped forms[8] and their structural characterization[9]. The purpose of the present paper is report for first time (to the best of my knowledge) the growth of single crystals of nickel doped potassium hydrogen tartrate (NPHT) in silica hydro gel at ambient temperature.

EXPERIMENTAL DETAILS

Crystal growth experiments are carried out in one open end corning glass tubes of length 15 cm and inner diameter 2.5 cm. The chemicals used are;

Commercial sodium meta silicate,

Tartaric acid-$C_4H_6O_6$ (analar BDH)

Nickel chloride-$NiCl_2 6H_2O$ (analar BDH)

Potassium Chloride-KCl (analar BDH).

The following chemical reactions are employed for the growth of NPT crystals:

Full Paper

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

The commercial sodium meta silicate is diluted with distilled water in 1:5 ratio and separate out the floating and suspended impurities by whatman filter paper no. 41. The double filtered solution is further diluted with requisite quantity of distilled water of gel sodium meta silicate (SMS) of varying specific gravity. Mixing sodium meta silicate solution of specific gravity 1.06 gm/cc with tartaric acid solution having different molar concentrations. The gel was set within 4 to 12 days depending on the gel density, pH of the gel solution and ambient temperature. After ensuring proper gel setting, the growth process was starting by adding a mixture of aqueous solution of $NiCl_2$ and KCl as the feed solution above the set gel with the help of a pipette. The details of crystal growth study are presented elsewhere[10].

The growth experiments are repeated by varying pH of gel 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. The grown crystals were characterized by chemical analysis, X-ray power diffraction and infrared spectroscopy.

RESULTS AND DISCUSSION

In terms of clarity of the crystals, separation between the crystals and form of the crystals, the combination of pH 2.5 to 3.0 gel mixtures and 0.5 M supernent feed solutions ($NiCl_2$ and KCl) gave the best results. The specific gravity of the sodium meta silicate solution used is 1.06 gm/cc. The gelling time is about 4 days. As the supernent solution diffused into the gel column a number of well defined regular as well as irregular shaped needle type transparent crystals (up to 2.9 cm in length) are observed as shown in Figure 1.

Still deeper in gel column where the diffusion rate attains a steady value, well developed bi-prismatic and hexagonal prism with rhombohedral edges transparent single crystals are grown. The typical single crystals are shown in Figure 2.

A habit of bi-prismatic and hexagonal prism with rhombohedral edges crystals are shown in Figure 3 and 4 respectively.

In gel growth, nucleation control can be achieved, to some extent by changing a variety of parameters viz., concentrations of feed solutions, gel density, gel pH, gel ageing and replenishment programmes. It is found that the pH values of 2.5 to 3.0 give optimum condition

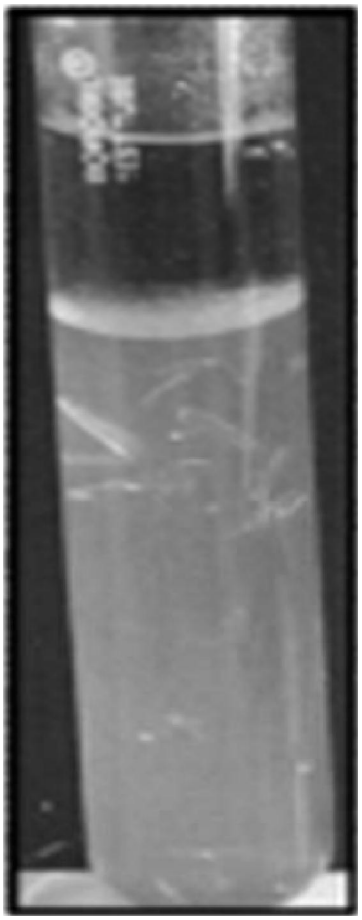


Figure 1 : Growth of nickel doped potassium hydrogen tartrate single crystals in the test tube.

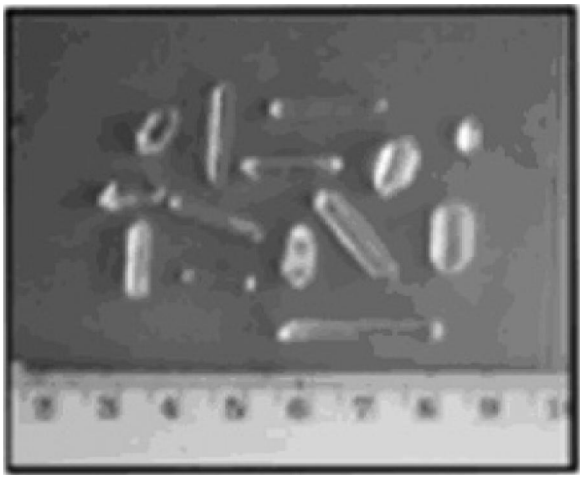


Figure 2 : Nickel doped potassium hydrogen tartrate single crystals.

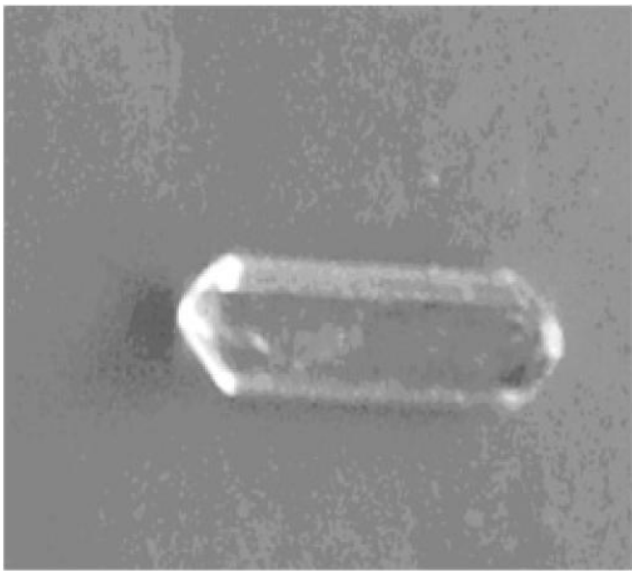


Figure 3 : Nickel doped potassium hydrogen tartrate bi-prismatic single crystal.

Figure 4 : Nickel doped potassium hydrogen tartrate hxagonal prism with rhombohedral edges single crystals.

for the growth of NPHT crystals. When the pH is increased above 3, irregular shaped and opaque needle type crystals are grown. On the other hand if the pH is decreased below 2.5, flower type dendritic crystals are formed. This may be due to the improper formation of cells at those pH values of gel.

It's observed that a very dense gel produces poor crystals. On the other hand, gels of insufficient density take a longer time to form and are mechanically unstable. It is also observed that nucleation density decreases as gel density increases. A greater gel density results in smaller pore size and poor communication among the pores thus decreasing the nucleation density at room temperature.

It is observed that longer a gel set, greater amount of water that evaporates out of the gel. The effect of the water evaporation should be considered before and after formation of gel framework.

Before the gel set, the evaporation of water causes an increase in gel density that in turn decreases the diffusivity of Ni^{2+} and K^{1+} ions in the gel thereby decreases number of nucleation sites. After the gel is set, evaporation of water 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 Ni^{2+} and K^{1+} ions and hence the number of nucleation centers. It is seen that as the concentration of the feed solution increases, the nucleation density also increases because of the enhanced availability of Ni^{2+} and K^{1+} ions. For the growth of good quality of crystals, suitable concentrations of feed solution are found to be 0.5 M. Similarly the concentration of tartaric acid, suitable for the growth of good quality crystals is 1.5 M.

The presence of Ni^{2+} and K^{1+} ions in NPHT crystals are confirmed by the usual chemical analysis and IPC method. It has been reported that the doping atom replaces the host one[9]. Carbon and Hydrogen elements are confirmed by C H N analysis. NPHT crystals contain 0.83 % nickel, 21.7 % potassium, 23.63 % carbon and 2.40 % Hydrogen.

An X-ray powder diffraction pattern of NPHT crystals was recorded by X-ray Powder Diffractometer, Model No. Xpert MPD DY 1152 with monochromatic

TABLE 1 : Indexed XRD data for nickel doped potassium hydrogen tartrate crystals

d value	2 θ	I/I_0	hkl
3.82928	23.20905	19.07	200
3.60071	24.70486	47059	210
3.1886	27.95884	11.07	211
2.84187	31.45319	22.36	220
2.4336	36.90507	22.58	310
2.372	37.89951	38.40	311
2.21368	40.72554	62.98	222
2.1709	41.56484	14.63	320
1.84573	49.33245	100.00	400
1.71941	53.2296	11.46	330
1.7015	53.84477	14.48	331
1.39698	66.92484	23.50	422
1.23723	77.01027	14.40	511
1.10513	88.37426	47.29	520

nickel filtered Cu Kα radiation (λ = 1.542 angstrom) as the X-ray source. The sample is scanned at a scanning speed of 2° per minute. The observed d values with relative intensities for these crystals are given in TABLE 1.

Infrared absorption spectra of these gel grown crystals were recorded on IR-435, Shimadzu Infrareds Spectrometer. The infrared spectra of these crystals are presented in Figure 5. The results obtained from IR Spectrum are summarized in TABLE 2.

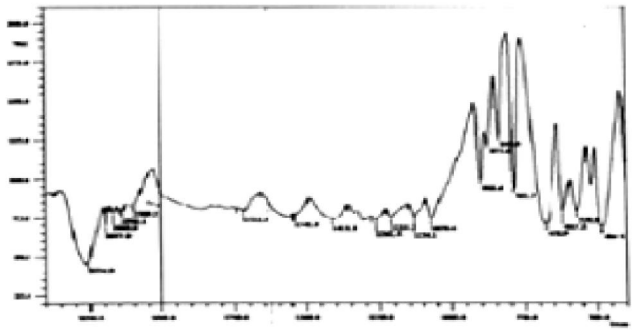


Figure 5 : IR spectrum of nickel doped potassium hydrogen tartrate single crystals.

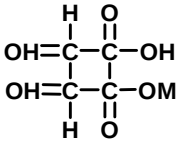
TABLE 2 : IR spectral data for nickel doped potassium hydrogen tartrate crystals.

Band (cm^{-1})	Assignment
3275 (s)	O-H stretching vibrations
2978 (s)	CH stretching
1772 (b)	C=O stretching vibrations
1541 (b)	CO system + δ O-C=O
1412 (b)	CO system + δ O-C=O
1261 (w)	OH in plane bending
1211 (w)	OH in plane bending
1134	Δ C-H, π C-H
1070 (s)	δ C-H, π C-H and CO stretching
484 (s)	M-O stretching

The peak 3275 cm^{-1} is due to strongly stretching modes of OH group. The bands due to CH stretching appear at 2978 cm^{-1}. The bands near 1772 cm^{-1} may be attributed to C = O of COOH group. While the band at 1412 and 1541 cm^{-1} are due to CO system + δ C – O = O modes. The band corresponding to 1211 and 1261 cm^{-1} may be attributed to OH in plane banding. Bands at 1070 and 1134 cm-1 indicate δ C – H and π C –H modes.

The plane bending band of the OH group in lattice ions at 1211 and 1261 cm^{-1} remains almost unchanged, so it indicate the non participation of OH group in the formation of band with metal ion. Besides, there are some peaks below 500 cm^{-1} indicates metal oxygen band.

The infrared spectral studies described above confirm the crystal structure for simple metal tartrate and represent schematically as below.



Where M = Ni or K

CONCLUSION

Transparent single crystals of NPHT can be obtained at a pH value 3.0 with gel density of about 1.06 gm/cc. Growth of the NPHT crystals is confirmed by relevant characterization techniques.

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 help and guidance.

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