Growth and Characterization of Silica Gel Grown Cobalt Tartrate Crystals

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ABSTRACT

The growth of cobalt tartrate crystals was achieved in silica gel by single diffusion method. The growth conditions were optimized by varying various process parameters such as pH of the gel solution, gel concentration, concentration of reactants etc. The test tubes were used as crystallization vessels, while silica gel as growth medium. Gel was prepared by mixing the solution of tartaric acid and sodium meta silicate. After setting of the gel, it was left for aging. After two or three day's duration, the supernatant zinc chloride of different molarities was poured over the set gel. After 48 to 60 hours of pouring the supernatant, small nucleation growth was observed below the interface of gel. Structural study was carried out by XRD; the thermal behavior of the material was studied using thermogravimetry (TG) and differential thermal analysis (DTA). It is observed that the material is thermally stable up to 30^0c beyond which it decomposes through many stages till the formation of cobalt oxide at 995^0c.

Keywords
Gel Grown Cobalt Tartrate Crystal, XRD, TGA/DTA, EDAX.

1. INTRODUCTION

One of the crystal growth methods at ambient temperature is gel method, developed at the end of the 19th century. Investigator Henischet.al [1] had been contributed large amount of efforts to formulate gel. His efforts are fundamental one to understand mechanism for the formation of gel. He could grow single crystals of calcium tartrate, calcium tungstate, Lead iodide etc. Number of researchers such as Kurutz et al,Joshi et.al, Byrappa et al, Saraf et al Bolotov et al [2-5] have been utilized the technique in various manners to grow single crystal of different materials.

The crystal growth is a heterogeneous chemical process in which conversion from one phase to another phase of a compound is involved. For the compounds of high melting point and insoluble in aqueous solutions, crystals can be grown from the melt at elevated temperatures. For the materials, which decompose before melting point at atmospheric pressure and for which a suitable solvent is not available, crystals of such material can be grown from gel technique. Crystal growth from aqueous solution is known from a long time, but control of heavy nucleation is a problem. Gel method is relatively simple and inexpensive. In the present investigation crystal growth by gel method is adopted.

Simplicity with which strain-free perfect crystals can be obtained at low temperature is the important aspect of this method. The principle role of gel medium appears to be suppression of turbulence, chemical inertness, permitting reagents to diffuse at a controlled rate and controlled nucleation. In addition, its softness and the uniform nature of constraining forces exerted upon the growing crystals, also encourage orderly growth. Its softness provide the space i.e. crucible for growing crystals.

Tartrate crystals are of considerable interest, particularly for basic studies of some of their interesting physical properties .Some crystals of this family are ferroelectric, some others are piezoelectric and quite a few of them have been used for controlling laser emission. As tartrates are sparingly soluble in water and decompose before their melting point. The gel method is found to be more promising than the high temperature crystal growth methods. Many tartrate salts with monovalent cations; such as rubidium hydrogen tartrate, sodium tartrate, cadmium tartrate, manganese tartrate, zinc tartrate and strontium tartrate have been studied for their dielectric and thermal properties.

Crystals are the unknown pillars of modern technology. The modern technological developments depend greatly on the availability of suitable single crystals, whether it is for lasers, semiconductors, magnetic devices, optical devices, superconductors, telecommunication etc. Unless the science of growing these crystals understood precisely, it is impossible to grow them as large single crystals to be applied in modern industry. The large number of crystals are used in electronic, optical and in industries. Hence today's demand is to grow large single crystals with high purity and symmetry. Hence the purpose of the present work is to report growth and influence of various parameters on the growth mechanism of crystals of strontium and zinc tartrate in silica gel at ambient temperature.

2. EXTERNAL

Crystals of cobalt tartrate were grown by single diffusion method .The details of various experiments on growth of these crystals have been published elsewhere. The experiments pertaining to the growth of cobalt tartrate crystals were conducted in borosilicate glass tube of 2.5 cm diameter and 20 cm length. Gel was prepared by mixing sodium meta silicate solution of specific gravity 1.04 gm/cm^3 with the desired concentration of tartaric acid (0.5 – 1.5M) which acted as lower reactant. The solution was continuously stirred to avoid local ion concentration which may cause premature local gelling and make the final solution inhomogeneous. The pH of the gel medium was adjusted between values of 3-5.The solution with the desired value of pH was then transferred to several glass tubes and left for gelling. After confirming the gel setting, an aqueous solution of cobalt chloride (0.2-1.5M) was carefully poured along the walls of the tube with the help of pipette over the set gel, in order to avoid any gel breakage. The cobalt ions diffuse through the narrow pores of the gel to react with the tartrate ions (C4H6O6-2) present in the gel as lower reactant giving rise to the formation of cobalt tartrate crystals.

The following reaction is expected to take place in the silica gel medium.

$$CoCl_2 + C_4H_6O_6 \quad \text{---------} \quad C_4H_6O_6 \, Co + 2HCl$$
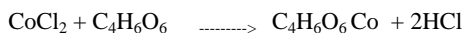
3. RESULTS AND DISCUSSION

Based on the various experiments conducted leading to pH of gel, gel density, concentration of upper reactant, concentration of lower reactant, gel aging etc. The best controlling parameters which lead to the growth of good cobalt tartrate crystals is obtained Table 1 shows the optimum conditions for growth of good tartrate crystals.

Table. 1. Optimum condition for growth of cobalt tartrate crystal

Various process parameter	Optimum conditions
Density of sodium meta silicate	$1.04 \, gm/cm^3$
Concentration of $CoCl_2$	0.5M
Concentration of $C_4H_6O_6$	0.9M
pH of Mixture	4.4
Temperature	Room temperature
Gel setting time	48hr
Gel aging time	36hr
Period of crystal growth	2weeks

Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel aging time, etc have considerable effect on growth rate. Near the interface of gel, dendrites growth is observed due to fast growth rate. However as the reactants percolates through the gel, the controlled reaction occurs below the depth of about 3cm.Hence good quality crystals having well developed faces are observed. In present work, figure.1.shows growth of cobalt tartrate crystals in test tubes, Figure 2 shows photo are the optical photographs illustrating varied morphology of cobalt tartrate. Figures 1 (a), (b) show crystals of cobalt tartrate grown for these different concentrations of supernatant (cobalt chloride,) ranging from 0.2M to 0.5M respectively. It is observed that as the concentration of supernatants increased from 0.2M to 0.5M, the size and the quality of the grown crystals also go on increasing. The crystals so formed are spherulite, star shaped, semitransparent and well isolated. Figure 2 (a) and (b) are the photographs illustrating varied morphology of cobalt tartrate [6-10].
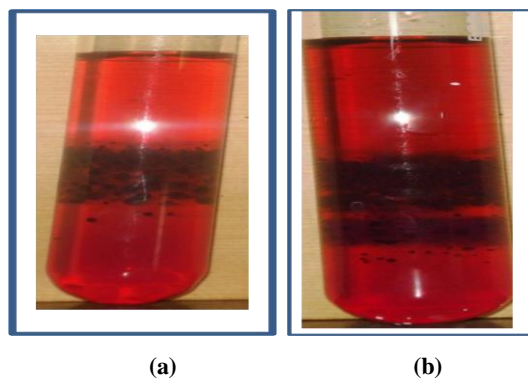

(a) **(b)**

Fig 1(a) & (b) cobalt tartrate crystals in silica gel at different concentrations of supernatant
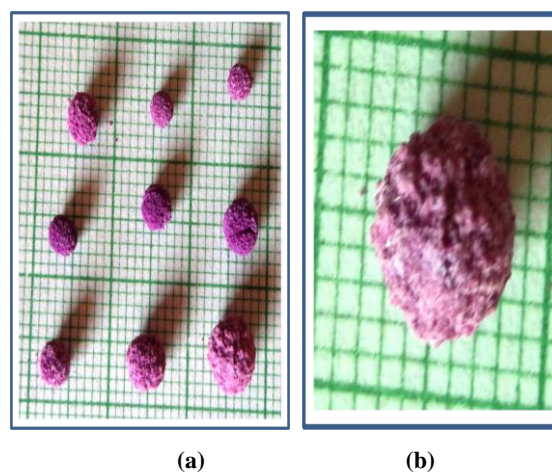

(a) **(b)**

Fig 2(a) Good quality cobalt tartrate crystals (b) Pink colored Spherulite shaped single crystal of cobalt tartrate

4. CHARACTERIZATIONS
4.1 X-ray Diffractometry (XRD)

The computer program, POWD (Interactive powder diffraction data and Indexing program version 23-0187) was used to calculate'd' and (hkl) values .
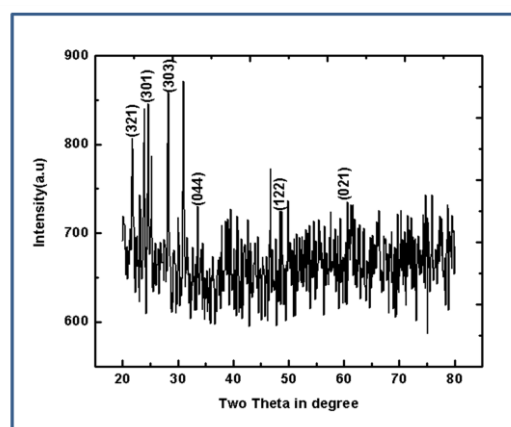

Figure 3 X-ray diffractogram of cobalt tartrate

The unit cell parameters and system calculated by the computer program are given in the table 2.These parameters satisfy the conditions for monoclinic system i.e. $a \neq b \neq c$ and $\alpha = \gamma = 900 \neq \beta$. Figure 3 shows x-ray diffractogram of cobalt tartrate crystal. From X-ray diffraction study it may be

concluded that the grown crystals of cobalt tartrate have monoclinic system [11-15].

Table 2 Calculated unit cell parameters

Lattice Parameters	cobalt tartrate
System	Monoclinic
a	$12.700 A^0$
b	$16.800 A^0$
c	$19.400 A^0$
$\alpha = \gamma \neq \beta$	90^0
V	4139.18

4.2 Thermal Analysis

Recrystallized alumina sample holders were used and the heating rate was $10^0C/min$. The thermograms were recorded in the temperature range from 30^0C to 1000^0C. The sample was hold for 1.0 min at 300C to evaporate water due to moisture and then heated from 30^0C to 1000^0C at $10^0C/min$. The experiment was carried out under a flow rate of 60 ml/min. in nitrogen atmosphere. Microcrystalline (powdered) samples of cobalt tartrate crystal were taken for thermal studies .The weight of the sample was 38.927mg for TGA/DTA.

4.2.1 Thermogravimetry Analysis (TGA)

The TGA curve for cobalt tartrate crystal is shown in figure 4. The percentages of the weight loss in the different stages of decomposition of cobalt tartrate are presented in table 3. There is a good agreement between the observed and calculated weight losses.

Cobalt tartrate is water coordinated compound. Therefore there is a possibility that this crystal may lose some of its water molecules while heating. TGA of cobalt tartrate showed clearly four stages of decomposition as expected, 1) Conversion of dehydration 2) Conversion of cobalt tartrate to cobalt oxalate 3) Conversion of cobalt oxalate to cobalt carbonate 4) Conversion of cobalt carbonate to oxides of cobalt. Observations are known from the literature on Rochelle salt and rare earth tartrates is reported by Kotru et al, Selvarajan et al, Yanes et al,Lopez et al. [16-19].

The first stage of decomposition ($30 – 115^0c$) results due to the elimination of water molecules. The calculated and observed mass losses corresponding to this are 21.50% and 21.7% of the total mass taken respectively. The second stage between $100^0C – 135^0C$ corresponds to the loss of oxygen and results in the formation of anhydrous cobalt tartrate. Then the compound is stable in the temperature range $135^0C - 340^0C$ so the thermograph is parallel to temperature axis. But in the range of temperature $340^0C – 410^0C$, loss of %weight is about 53%. Then the compound slowly decomposes in the temperature range $480 – 995^0C$ and % weight loss is 6%.

Table 3 TGA data of cobalt tartrate

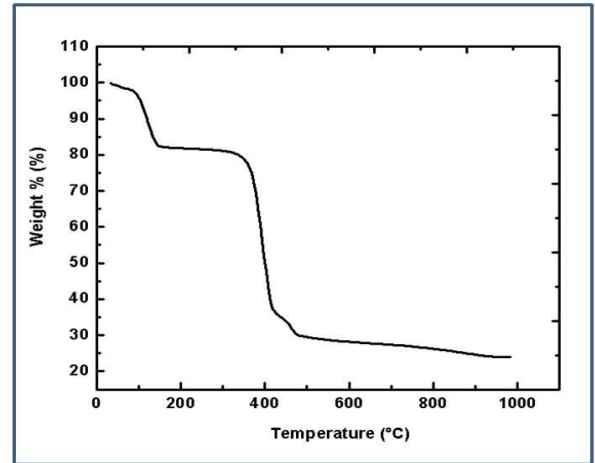| Stage	Temperature range	Observed % weight loss	Calculated % weight loss
I	$30 – 115^0C$	21.5	21.7
II	$340 – 410^0C$	53.0	53.2
III	$410 – 995^0C$	6.0	6.1

Figure 4 TGA curve for cobalt tartrate

4.2.2 Differential Thermal Analysis (DTA)

The DTA curve for gel grown cobalt tartrate crystals is as shown in the figure 5 and the DTA data collected from this curve is tabulated in the table 4.

In DTA curve we observe three endothermic peaks at 120^0C, 390^0C and 475^0C.The endothermic peaks at 120^0C, 390^0C, and 475^0C are due to the decomposition of hydrated cobalt tartrate into anhydrous cobalt tartrate. In the first stage of decomposition, peak at 120^0C is attributed to the loss of first water molecules immediately followed by another endothermic peak at 390^0C which corresponds to loss of water molecules again. The endothermic peak at 475^0C is due to formation of anhydrous cobalt tartrate. This endothermic peaks observed in the DTA curve corresponds to the total weight loss of water molecule in the TG curve.
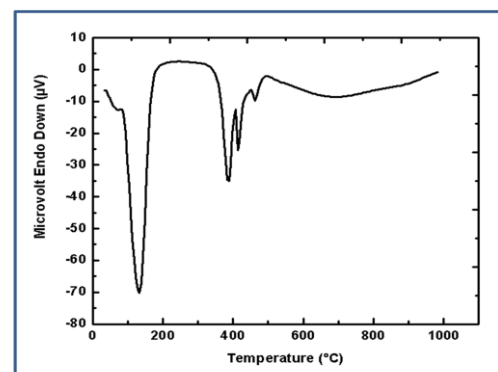

Figure 5 DTA curve for cobalt tartrate

Table 4 DTA data of cobalt tartrate

Peak Temperature in ^{0}C	Nature of reaction
120	Endothermic
390	Endothermic
475	Endothermic

4.3 Energy Dispersive Analysis by X-rays (EDAX)

Energy Dispersive analysis by X-rays (EDAX) is used for the quantitative analysis and is also called as elemental analysis. Figure 6 shows EDAX spectrum of tartrate as reported by Girase et al, Indulal et al, Garud et al, Patil, Pandita et al [20-22]. EDAX-carried out standard less at 10KeV energy showed the following results for the given sample of cobalt tartrate crystals. The peak ranging from6.8KeV to7.2KeV clearly indicates the presence of cobalt in the sample; it also gives the 1200 counts per second. The relative concentration of the cobalt is observed as 85.0%. All these observations after analyzing, the EDAX lead to the conclusion that the sample crystal shows presence of cobalt. Table 5 shows result of elemental analysis.

Table 5 Result of elemental analysis

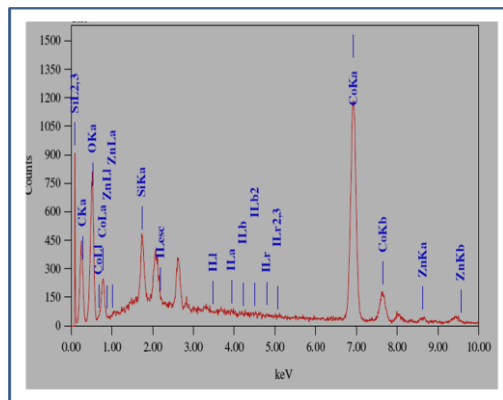| Element	Theoretical value %	Practical Value %
Co	6.76	6.6

Figure 6 EDAX spectrum of cobalt tartrate

5. CONCLUSIONS

1. Good quality cobalt tartrate crystal can be grown by gel method.
2. The 'd' values of grown material obtained from the XRD matched well with the values obtained by POWD Programme (JCPDS card no.2.2).
3. Water of crystallization present in grown crystals, is confirmed by TGA / DTA,
4. The EDAX studies suggested that grown crystals are of cobalt tartrate indeed.

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