

FT-IR, Thermal and Optical Studies of Gel Grown Cobalt Tartrate Crystals

S.J. Nandre^{1,*}, S.J. Shitole^{2,†}, R.R. Ahire³

¹ Department of Physics, Uttamrao Patil College, Dahivel, Tal. Sakri, Dhule, 424304 India

² Department of Physics, Z. B. Patil College, Dhule, 424002 India

³ Department of Physics, S. G. Patil College, Sakri, Dhule, 424304 India

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The growth of cobalt tartrate crystals was achieved in silica gel by single diffusion method. Optimum conditions were established for the growth of good quality crystals. Fourier transform infrared (FT-IR) spectroscopic study indicates the presence of water molecules and suggests that tartrate ions are doubly ionized. The thermal behavior of the material was studied using thermogravimetry (TG) and differential thermal analysis (DTA). The results show that the material is thermally stable up to 30 °C, beyond which it decomposes through many stages till the formation of cobalt oxide at 995 °C. The non linear optical behavior of these crystals is reported and explained.

Keywords: Gel grown cobalt tartrate crystals, FT-IR, TGA / DTA, UV spectroscopy.

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1. INTRODUCTION

Tartaric acid is a common byproduct of the wine industry may serve as a base for the two hydroxyl as well as two carbonyl groups and in this compound permits ready incorporation of phosphorus containing moieties. For most applications, these materials are used for their dielectric, ferroelectric and piezoelectric or non linear optical properties [1-3]. These characteristics of tartrate compounds are utilized for their use in transducers, linear and non linear mechanical devices. Several researchers have grown materials of great interest from both solid state sciences as well as technological point of view in single crystal and polycrystalline form by gel technique [4], and modified such materials by suitable substitution to determine the effect of modification of composition on their characteristics [5-8]. In the recent years the technology and science of crystal growth has advanced rapidly for the development of new nonlinear optical materials. The desire to utilize the properties of these materials in applications such as telecommunications, optical data storage and optical information processing has created a need for new materials with very large second order susceptibilities [9-12]. Most commercial materials are inorganic especially for high power use [13]. Inorganic materials were mainly grown by solution growth techniques. One of the possibilities to grow single crystals of sparingly insoluble inorganic substance is the use of gel method [14-17].

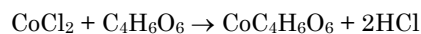
The present work describes the growth of cobalt tartrate crystals grown in silica gel. These crystals are identified and characterized by FT-IR, thermogravimetry (TGA) and differential thermal analysis and UV absorption spectroscopy.

2. MATERIALS AND METHODS

Spherulitic crystals of cobalt tartrate were grown by single diffusion method. The details of various experiments of 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 metal silicate solution of specific gravity 1.04 gm / cm³ with the desired concentration of tartaric acid (0.5-1.5 M) 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 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 (0.2-1.5 M) 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 (C₄H₆O_{6,2-}) 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 gel medium.



Based on the various conducted experiments 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 growth of good cobalt tartrate crystals are given in table 1 which shows the optimum condition to grow the good tartrate crystals.

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 reactants, dendrite 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 3 cm, hence good quality, well developed faces of crystals are observed.

* sjnandre@gmail.com

† sjshitole@hotmail.com

In present work, figure 1 shows tartrate crystals in test tubes, figure 2 shows optical photo graph of cobalt tartrate crystals under variation of upper reactant conc. 0.5 M. Figure 3 illustrates different morphologies of pure cobalt tartrate crystals.

Table 1 – Optimum condition for growth of cobalt tartrate crystals

No	Various process parameters	Optimum conditions
1	Density of sodium meta silicate	1.04 gm/cm ³
2	Concentration of CoCl ₂	0.5 M
3	Concentration of C ₄ H ₆ O ₆	0.9 M
4	pH of Mixture	4.2
5	Temperature	Room temperature
6	Gel setting time	48 hrs
7	Gel aging time	36 hrs
8	Period of crystal growth	2 weeks



Fig. 1 – Cobalt tartrate crystals in test tubes



Fig. 2 – Cobalt tartrate crystals under variation of upper reactant conc. is 0.5 M



Fig. 3 – Different morphologies of pure cobalt tartrate crystals

3. RESULTS AND DISCUSSION

Cobalt tartrate crystals were characterized by FT-IR, thermal analysis, and UV spectroscopy.

3.1 Fourier Transform Infrared (FTIR) Spectral Analysis

In organic chemistry, an IR spectrum is used for qualitative and quantitative analysis. The FT-IR spectrum of cobalt tartrate was recorded in KBr phase in frequency region 400-4000 cm⁻¹ using SHIMADZU spectrometer. Figure 4, shows FT-IR spectrum of cobalt tartrate. The recorded FT-IR spectra were compared with the standard spectra of functional groups [18]. The broad band due to stretching vibrations of hydroxyl, water and C-H groups is observed. FT-IR spectral and vibrational assignments of cobalt tartrate are shown in following table 2.

Table 2 – FT-IR spectral and vibrational assignment of cobalt tartrate crystals

No	Wave number cm ⁻¹	Intensity	Assignments
1	3640-3610	S, Sh	O-H Stretch
2	3100-3000	S	C-H Stretch
3	3000-2850	M	C-H Stretch
4	2830-2695	M	C-H Stretch
5	2260-2100	W	C = C Stretch
6	1650-1580	M	N-H bend
7	1470-1450	M	C-H bend
8	850-550	M	C-Cl stretch

M = medium, W = weak, S = strong, B = broad, Sh = sharp.

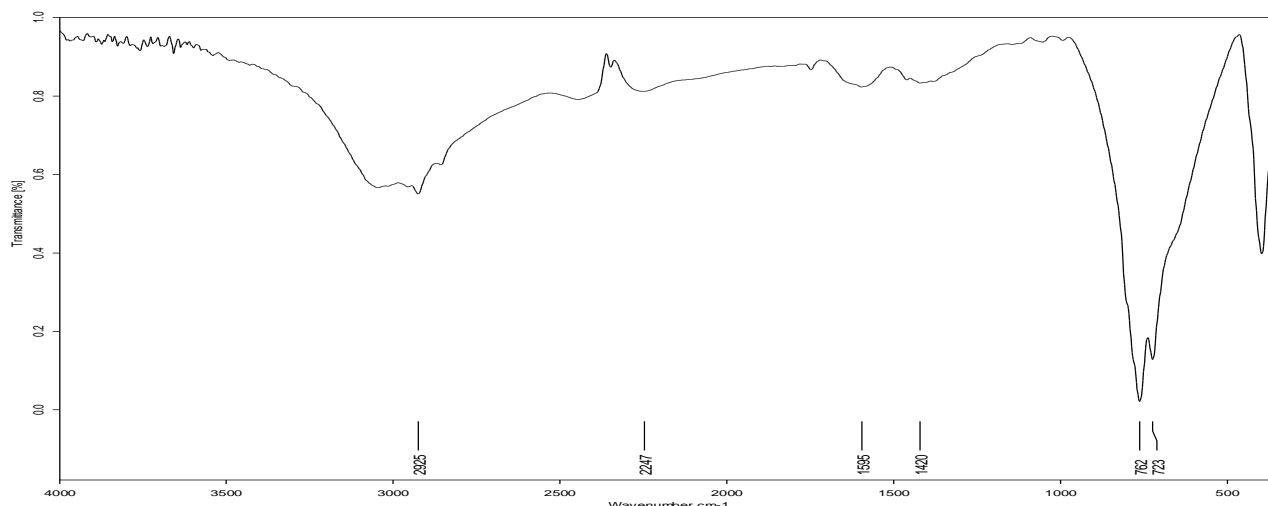


Fig. 4 – FT-IR spectrum of cobalt tartrate crystal

3.2 Thermal Analysis

Thermal studies give useful information regarding the thermal stability and composition of the sample under investigation. Recorded curves were first analyzed for obtaining the percentage mass loss at different temperatures and hence about the thermal stability and dissociation of the compound [19-20].

The TG /DTA curve of cobalt tartrate is obtained at the temperature range 30-1010 °C. As indicated, the material remains stable up to the temperature 30 °C and starts decomposing about at 35 °C and the process continues up to 995 °C, after which it is reduced to oxide. Figure 5 represents the TGA curve and figure 6 represents the DTA curve.

TGA

The TGA curve for cobalt tartrate crystal is shown in figure 5. The percentages of the weight loss on the different stages of decomposition of cobalt tartrate are presented in table 3.

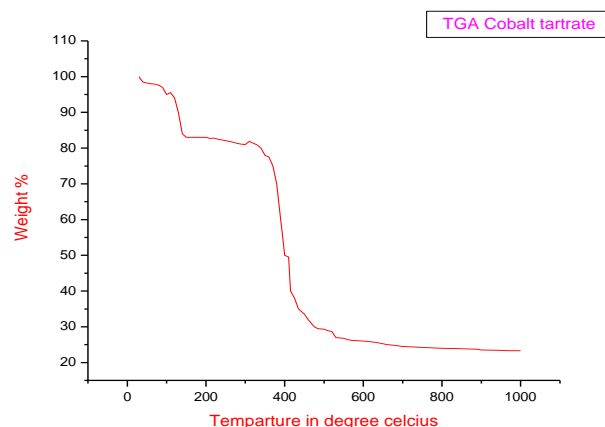


Fig. 5 – TGA curve of cobalt tartrate crystal

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) 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.

Table 3 – TGA data

No.	Temperature range	Observed % weight loss	Calculated % weight loss
I	30-115 °C	21	20.7
II	340-410 °C	38	38.2
III	410-995 °C	33	33.1

The observations of Rochelle salt and rare earth tartrates are known from the literature. The first stage of decomposition (30-115 °C) 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 is between 100-135 °C and corresponds to the loss of oxygen and results in the formation of cobalt oxalate. Then the compound is stable at temperature 135- 340 °C, the thermograph is parallel to temperature axis. But in the range of temperatures 340-410 °C it loses % weight about 53 %, and the formed product is cobalt carbonate.

Then the compound slowly decomposes at the temperature range 480-995 °C and % weight loss is 6 %, forming oxides of cobalt. TGA data is shown in table 3.

DTA

The DTA curve for cobalt tartrate gel grown crystals is shown in figure 6 and the DTA data collected from this curve is tabulated in table 4.

In DTA curve we observed three endothermic peaks at 120 °C, 390 °C, and 410 °C. The endothermic peak at 120 °C, 390 °C and 410 °C are due to the decomposition of hydrated cobalt tartrate into anhydrous cobalt tartrate. On the first stage of decomposition, the peak at 120 °C is attributed to the loss of first water molecules and is immediately followed by another endothermic peak at 390 °C which corresponds to loss of water molecules again.

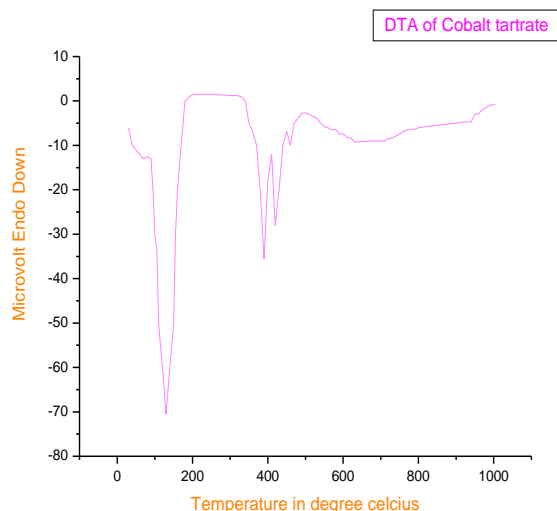


Fig. 6 – DTA curve of cobalt tartrate crystal

Table 4 – DTA data

No	Peak Temperature in °C	Nature of reaction
1	120	Endothermic
2	390	Endothermic
3	410	Endothermic
4	475	Endothermic

The endothermic peak at 475 °C is due to decomposition 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.

4. UV ABSORPTION SPECTROSCOPY

The absorption spectra of cobalt tartrate crystals were recorded using a SHIMADZU UV-2450 UV-Vis spectrophotometer over the wavelength range 200-650 nm. Figure 6 shows UV absorption spectra of cobalt tartrate crystals. From the spectrum, it has been inferred that cobalt tartrate crystals have sufficient transmission in the entire visible and IR region. The absorption coefficient is high at lower wavelength and wide transparency from 430 nm suggesting their suitability for second and third harmonic generations of the radiation [21-23].

The band gap energy of cobalt tartrate crystals with the obtained wavelength is calculated using the following simple conversion equation.

$$\text{Band gap energy (eV)} = 1240 / \text{wave length (nm)}$$

Band gap energy is represented in table 5.

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Table 5 – Band gap energy of cobalt tartrate crystal

Crystal	λ (nm)	Band gap Energy (eV)
Cobalt tartrate	300	4.13

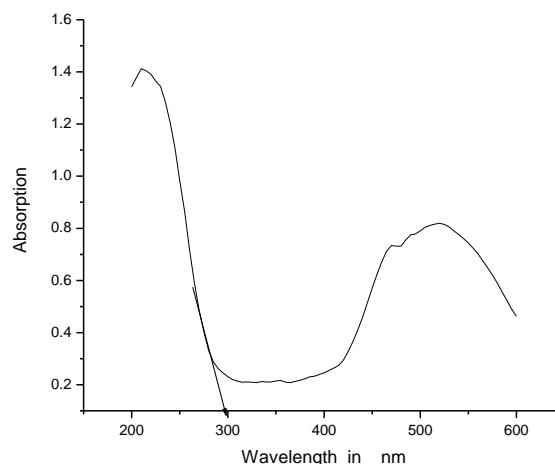


Fig. 6 – UV of cobalt tartrate crystals

5. CONCLUSIONS

i) Single crystal of cobalt tartrate was grown by the gel growth technique.

ii) Cobalt tartrate crystal has different morphologies. Some of the crystals are opaque and few good quality crystals were obtained.

iii) The FT-IR spectrum confirms the formation of cobalt tartrate crystals.

iv) The result of thermal analysis suggests that the gel grown cobalt tartrate is thermally unstable even at low temperature. Decomposition starts at about 30 °C and process continue up to 995 °C, after which it reduces to oxide. Finally, cobalt tartrate decomposes to cobalt oxide.

v) It has been inferred that cobalt tartrate crystal has sufficient transmission in the entire visible and IR region.

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