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## Powder XRD, FT - IR and Thermal Study of Copper Tartrate Crystals

### ABSTRACT

*Copper Tartrate crystals were grown by single diffusion gel growth technique. Optimum conditions were established for the growth of good quality crystals. Grown crystals were characterized by powder XRD, FT-IR and TG-DTA-DSC. Grown crystals shows O-H, C=O, C-O, C-H and Metal Oxygen Bonds. Crystals were thermally stable up to 111 oC. Copper tartrate crystals shows orthorhombic crystal system.*

### [1.0] INTRODUCTION :

Tartaric acid, a common byproduct of the wine industry, may serve as a base for the development of new class of materials. The presence of the two hydroxyl as well as two carbonyl groups in tartaric acid permits the ready incorporation of monovalent, divalent or trivalent metal ions as well as incorporation of phosphorus-containing moieties. Mainly tartrate crystals possess application, as dielectric, ferroelectric and piezoelectric materials or show non-linear optical properties [1-3]. These characteristics of Tartrate compounds are utilised for their use in transducers, linear and non-linear mechanical devices [2]. Sodium Tartrate Dihydrate is commonly used as primary standards for methods that determine water contents [4]. Lanthanides form a series of compounds with properties that change regularly with increasing atomic number of lanthanide [5].

For the materials which show poor solubility in water and which decompose before melting and do not vapourise or sublime on heating, the gel method offers an attractive advantage for their synthetic crystallization [6]. 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 [7] and modified such materials by suitable substitution to determine the effect of modification of composition on their characteristics [8-10]. Thermal stability of phosphinated diethyl tartrate which is flame retardant has been reported [11,12].

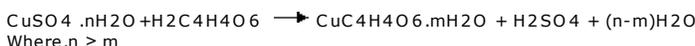
Some tartrate compounds are used in military applications. Strontium Tartrate is used in ammunition units [13] Manganese tartrate crystal being temperature sensitive can be used to sense and measure the temperature. A wax pencil is developed to sense the surface temperature of heated substance in terms of change in the coloration upon contact. The change in coloration of this crystal occurs at 410oC from pink to black. The coloration change is almost instantaneous and occurring within 1 to 2 seconds. Gvozdoz and Erunov [14] described this method. The effect of light on copper tartrate has been examined [15]. Copper tartrate has shown in vitro to stimulate Luteinizing hormone. Clomitol is the drug used to add a specific type of copper to the testosterone regulating mineral complex [16]. The synergist effect of tartaric acid for zinc ion in cosmetics has been reported [17]. Zinc tartrate and zinc tartrate with other compounds form a bright coating and used as protecting powder for metals [18].

In the present investigation, the authors have grown prismatic crystals of copper tartrate. The results obtained by powder X-ray diffraction (XRD) studies, Fourier transform infra-red spectroscopy (FT-IR) and thermogravimetric analysis (TG- DTA -DSC).

### [2.0] EXPERIMENTAL :

#### [2.1] Growth Procedure

The apparatus used for crystallization of single crystals of pure and modified copper tartrate by gel technique consists of borosilicate glass tubes of length 20cm and diameter 2.5cm placed vertically on a wooden stand. Silica gel was prepared by adding a solution of sodium meta silicate to tartaric acid slowly with continuous stirring to avoid any local ion concentration, which would otherwise cause premature local gelling and make the final solution inhomogeneous. A fixed amount of gel solution with 1.04 g/cm<sup>3</sup> specific gravity and value of pH was set at 4.0 by adding 1M solution of tartaric acid transferred to several test tubes. The test tubes were sealed with some suitable material to prevent fast evaporation and contamination of the exposed surface of the gel. The gel setting time was found to be strongly dependent on pH and environmental temperature. After confirming the gel setting, an aqueous solution of copper chloride of a particular molarity was poured over the gel carefully along the walls of the test tube so as to avoid any gel breakage. The following reaction is expected to take place leading to the formation of copper tartrate crystals:



To grow copper tartrate crystals, copper sulphate solution was poured on the gel. The diffusion of  $\text{Cu}^{2+}$  ions through the narrow pores of the silica gel leads to the reaction between these ions and the  $\text{C}_4\text{H}_4\text{O}_6^{2-}$  ions present in the gel. The reaction leads to the formation of copper tartrate crystals as per above chemical reaction.

#### 2.1 Characterization Techniques

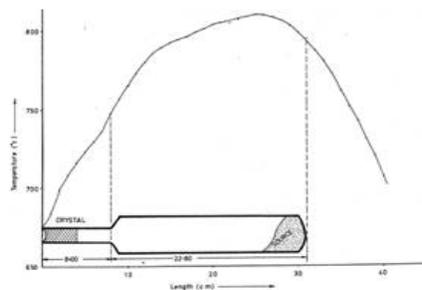
In the present investigation, an attempt is made to find out the cell parameters of copper tartrate crystals and compare the same with the reported values. Using DEBYE computer programme,  $h$ ,  $k$  and  $l$  parameters as well as  $d$  and  $2\theta$  values are generated in such a way that these values match with the X-ray powder diffraction values, then by using the programme REFEDT.BAS. the new values of  $a$ ,  $b$ , and  $c$  are generated from the  $h$ ,  $k$ ,  $l$  and  $d$  values obtained earlier. FT-IR spectrum was recorded by using Nicolet (Thermo Scientific) - 6700 set up in the range from 400  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  in KBr medium. The TGA, DTA, DSC was carried out on LINSEIS STA PT -1600 from room temperature to 900oC at a heating rate of 15 oC/min.

### [3.0] RESULT AND DISCUSSION

#### [3.1] Growth Observations

After adding 1 M  $\text{CuSO}_4$  supernatant solution on set gel, a 1 cm thick band of small crystals was observed after one day. This band further fattened to 1.7 cm and a few scattered crystals began to grow below it after two days. After four days the band extended to 2.2 cm width, the density of number of crystals decreased on moving towards the bottom. After six days the band increased up to 2.9 cm width and a few large size crystals were grown in the lower region of the band. This band was further swollen to 3.2 cm and 3.6 cm after nine days and eleven days, respectively. After fifteen days it expanded to 3.8 cm and more crystals were found to be growing in the lower part of the test-tube. Some crystals had apparent dimension up to 4 mm. Fig. 1 (a) shows the grown copper tartrate crystals in test tube and Fig. 1 (b) shows the magnified



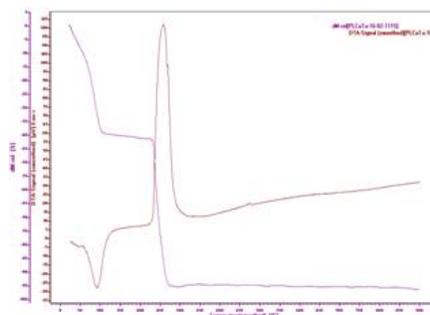


**Fig. 4: FT-IR spectrum of copper tartrate crystals**

It can be observed from fig. 4 that the the O - H stretching is clearly observed in the form absorption around 3260  $\text{cm}^{-1}$ . The C = O stretching due to carbonyl group is observed around 1600  $\text{cm}^{-1}$ . The O - H out of plane bending is seen around 1050  $\text{cm}^{-1}$ . The C - O stretching vibration is observed around 1380  $\text{cm}^{-1}$ , 1236  $\text{cm}^{-1}$ . The C - H stretching is also observed around 1103  $\text{cm}^{-1}$ . Presence of Metal Oxygen bonding is clearly shown from the absorption between 900  $\text{cm}^{-1}$  to 450  $\text{cm}^{-1}$ .

#### [3.4] TG-DTA-DSC

Thermogravimetric analysis (TG) is a very useful technique to assess the thermal stability of various substances. Many authors have reported TGA for various tartrate crystals. Selvarajan et al. [23] studied the thermal properties of calcium tartrate single crystals using TGA. Thermal properties of gel grown pure and nickel doped strontium tartrate tetrahydrate single crystals were studied by Rethinam et al. [24]. Ramkrishnan [25] reported TGA studies on manganese tartrate trihydrate crystals, whereas, the thermal study on rare earth pure and mixed tartrate crystals was reported by Kotru et al.[26-27]. Moreover, the TGA study was reported on iron (II) tartrate crystals by Joseph et al. [28] and on calcium tartrate crystals by Joshi and Joshi [29]. Recently, thermal decompositions of Bi (III), Cd (II), Pb(II) and Cu (II), Thiocyanates have been reported by Ptaszynski et al.[25]



**Fig. 5: TG - DTA curve of copper tartrate crystals**

Fig. 5 shows the decomposition of hydrated copper tartrate crystals. At 111 $^{\circ}\text{C}$  hydrated copper tartrate crystals first decompose into anhydrous form. After that it decomposes very slowly and then a sharp decomposition takes place around 232 $^{\circ}\text{C}$  and  $\text{CuO}$  is formed at 275 $^{\circ}\text{C}$ . The DTA - DSC peak shows that first decomposition in the form of endothermic reaction is observed at 90.1 $^{\circ}\text{C}$ . This shows the dehydration of copper tartrate. Thermodynamic parameters for this reaction are Enthalpy,  $\Delta C_p$  (change in heat capacity) and Heat Change are -668.90 J/g, 3.7405 J/gK and -269.35  $\mu\text{Vs/mg}$ . An Exothermic reaction is observed around 258 $^{\circ}\text{C}$ , which may be due to formation of gaseous products from copper tartrate. Thermodynamic parameters for this reaction are Enthalpy,  $\Delta C_p$  and Heat Change are 2669.47 J/g, 1.8709 J/gK and 1217.97  $\mu\text{Vs/mg}$ .

#### [4.0] CONCLUSION :

Bluish prismatic crystals were grown by single diffusion gel growth technique. Gel pH was set at 4.0 by adding appropriate amount of tartaric acid in the solution of sodium meta silicate. After setting the gel solution of copper chloride was poured on set gel, after 15 days full grown crystals were obtained inside this gel. Powder XRD confirms the orthorhombic crystal system of the grown crystals. FT-IR confirms the O-H, C=O, C-O, C-H and Metal Oxygen bonds. TG shows that the crystals remains stable up to 111  $^{\circ}\text{C}$  and DTA study shows an endothermic reaction at 90.1 $^{\circ}\text{C}$  and an exothermic reaction at 258 $^{\circ}\text{C}$ .

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