

Synthesis and characterization of copper tartrate Crystals grown in silica gel

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Abstract

Copper tartrate crystals were grown by the 'Single diffusion' method in silica gel by gel growth technique. Optimum conditions of crystal growth such as pH, specific gravity, aging period of gel, concentration of reactants in gels were determined by varying them. The unit cell of a grown crystal is Orthorhombic as characterized using Powder X-Ray diffraction. The Fourier transform infrared spectrum in the range 400–4,000 cm⁻¹ were recorded and the vibrational bands corresponding to functional groups is assigned. FTIR has confirmed the carboxyl as functional group and the other bonds between atoms. XPS has concluded paramagnetic nature and the presence of cu²⁺ ion.

Keywords: PXRD; FTIR; Copper Chloride; Tartaric acid; Sodium Meta Silicate; XPS

1. Introduction

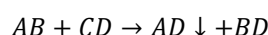
Wide variety of materials in single crystalline form have been synthesized in Silica gel at ambient temperature using cost effective equipment [1,2,3]. Copper tartrate have been reported to be grown in silica gel [4,5,6,7] find applications related to electrical, magnetic, Opto-electronic and medicinal properties and the same has been selected for synthesis and further investigation.

The gel medium prevents turbulence and being chemically inert, it provides a three-dimensional crucible which permits the reagents to diffuse at a desirable controlled rate. Its softness and uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth [8]. The growth of single crystals in gel at ambient temperature, which are sparingly soluble in water, is a fascinating alternative to the techniques involving high temperature and expensive equipment [1]. Out of the four basic techniques to grow crystals using the gel-growth method the technique mostly used to grow crystals of new compound in a test tube is by 'single diffusion' and 'Chemical Reaction Method' [2].

In this 'Chemical reaction method' two soluble reactants are allowed to diffuse through a gel where they react and form an insoluble or relatively less soluble crystalline product.

This method consists of having compound A inside the gel, and a solution of salt B is poured onto the top of the gel. When the diffusion of B throughout the gel is happening, the crystallization process of compound C takes place inside the gel network; this C compound is not soluble in water if the gel is a hydrogel [9].

The reaction mechanism can be shown as,



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In this study, crystalline product copper tartrate ($CuC_4H_4O_6$) is formed from diffusion of reactants Copper Chloride and tartaric acid in Silica gel. The silica gel is obtained by the acid neutralization of the sodium metasilicate [10]. Inorganic gels from salts have been studied for a long time. Graham [11] showed that the water in silica gel could be exchanged for organic solvents, which argued in favor of the theory that the gel consisted of a solid network with continuous porosity. The network structure of silica gels was widely accepted in 1930s, largely through the work of Hurd, who showed that they must consist of a polymeric skeleton of silicic acid enclosing a continuous liquid phase [12].

Gel method allows effective control over factors such as density, concentration, and pH [13].

As a general rule, the denser the gel, the poorer are the resulting crystals and the more contaminated with silicon. It is therefore desirable to work with the lowest gel concentrations which can be conveniently handled, bearing in mind that very dilute gels take a long time to set. Silica gel concentrations of specific gravity between 1.035 and 1.40 g/cm³ appear to represent a practical limit [14].

Under the most conditions, the shape (i.e., the habit) of a crystal is determined by kinetics rather than thermodynamics and the resulting habit is termed the "growth" as opposed to the "equilibrium" habit [15].

In this study parameters of crystal growth in gel such as specific gravity of silica gel, concentration of reactants, aging and pH of gel were varied to determine optimum conditions for crystal growth.

2. Material and methods

2.1. Crystal Growth

Copper tartrate ($CuC_4H_4O_6$) crystals were grown by the gel growth method in silica gel by single diffusion technique. Copper Chloride ($CuCl_2 \cdot 2H_2O$) is used as a supernatant or outer reactant. Sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) is used to prepare silica gel by neutralization method with acid as Tartaric acid ($C_4H_6O_6$). Tartaric acid is used as an inner reactant. All chemicals were of analytical grade.

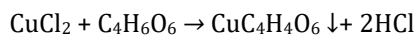
Sodium metasilicate solution of 1M is prepared in deionized water. Specific gravity of silica gel was measured. For silica gel setting 1 M sodium metasilicate solution was added to a 1 M tartaric acid solution in a test tube until the pH value reached 4.0 and poured into a round bottom cylindrical test tube of size 1.8 cm x 15 cm with flat circular bottom. Test tube is sealed for gelation. After the firm gel setting, 1 M aqueous solution of copper chloride was poured on top of the gel dropwise (along the walls of the tube to avoid any gel breakage) and allowed to diffuse into the gel in a sealed airtight test tube. Within a day, pure copper tartrate crystals of bluish color were seen growing and within 30-45 days crystal growth is complete any gel holding the bluish crystals is seen in the test tube as in figure 1.



Figure 1 Crystal Growth of Copper tartrate in Silica gel

Silica gel of lower specific gravity is weak to hold the crystals. At high specific gravity, gel is rigid. At high aging time, pore size decrease which reduce number of crystals. At critical aging time in days, crystals of optimum size can be grown at certain pH of a gel and concentrations of inner and outer reactants. Diffusion of copper ions and tartrate ions lead to mass transport and react to produce bluish copper tartrate crystals, moderately transparent and prismatic copper tartrate crystals. The size of crystal grown is 3 mm x 3 mm x 1mm for 1M concentration of each reactant.

The chemical reaction inside the silica gel growth for the formation of the crystal can be represented by,



Higher aging time in days reduce pore size and nucleation density. At high pH quality of crystal is not good. At pH value of four and aging of 4 days after firm gel setting crystal growth has been found better. The optimum growth conditions determined in this study is presented in the table 1 below.

Table 1 Optimum conditions of copper tartrate Crystal growth

Sr No	Specific parameter	Optimum value
1	Specific gravity of Silica gel	1.04 g/cc
2	pH of gel medium	4.00
3	Concentration of inner reactant 'tartaric acid'	1M
4	Concentration of outer reactant 'Copper Chloride'	1M
5	Gel setting time	24 Hr -36 Hr
6	Growth period	1½ month
7	Gel Aging	4 days after Gel Setting

2.2. Characterizations

The crystal structure and elemental composition of the grown crystals were determined by characterization techniques presented in following discussion:

2.3. X-ray Powder Diffraction:

The grown copper tartrate crystals were characterized by Powder X-ray diffraction (PXRD). PXRD was performed by instrument Benchtop (B2)/250242 with copper K_α radiation of wavelength 1.54060 Å. The PXRD has been recorded reflections from angle(2θ) in the range 5.002° to 49.998° . The powder XRD pattern of copper tartrate is shown in Figure 2. The peaks are indexed by the method of least- squares fit from the XRD data as represented in Table 2. The calculated unit cell dimensions data from observed data has concludes that the crystal is found to be crystallized in the orthorhombic structure with lattice parameters $a = 8.6716637 \text{ \AA}$, $b = 11.76998 \text{ \AA}$, $c = 9.20782$ and $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$, which are in agreement with the reported [7 ,6] and intensities are matched COD ID 7023997 [16].

Table 2 PXRD Data of Copper tartrate

$2\theta^\circ$	d (Å)	Indices of Plane (h, k, l)
11.5870	7.63119	011
12.3740	7.14750	110
15.0420	5.88499	020
19.2630	4.60391	002
20.2850	4.37429	121
21.6550	4.10057	210
24.9010	3.57295	130
25.3160	3.1520	220
30.5710	2.92188	003
36.7870	2.44121	321
35.2420	2.54459	240

The volume of unit cell of copper tartrate crystal is 933.835474 \AA^3 with space group P 21 21 2.

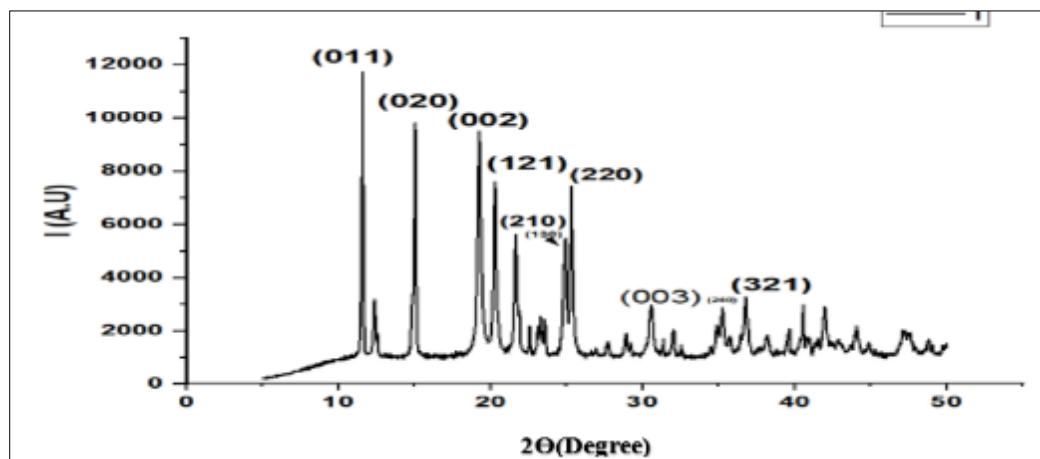


Figure 2 PXRD Pattern Peak Data of Copper Tartrate

2.3.1. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) by K ALPHA+ made at M/s Thermo Fisher Scientific Instruments.

The copper 2p scan electron binding energy spectrum of copper tartrate is shown in Figure 3.

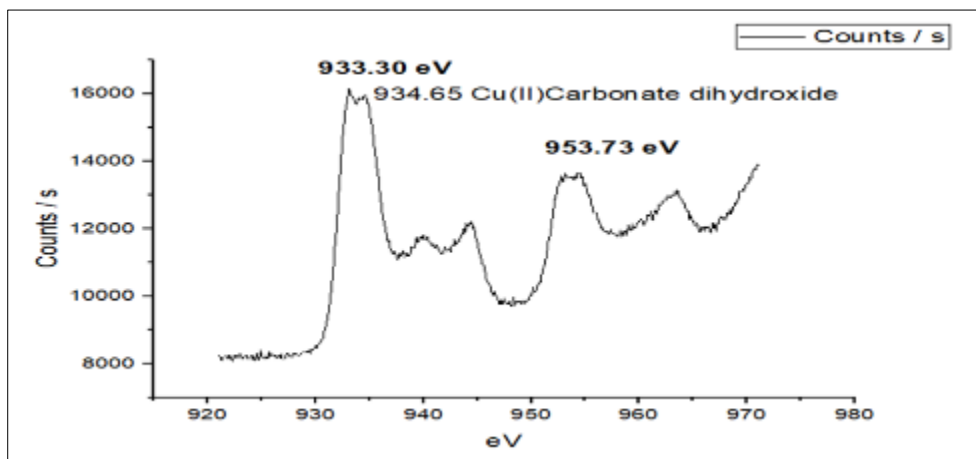


Figure 3 Cu2p Scan of Copper tartrate single crystal

The binding energy peak of 2p_{3/2} peak at 933.30 eV is observed. The spectrum consists of spin-orbit-split 2p_{3/2} and 2p_{1/2} peaks and satellites. These peaks seem to be sensitive in deducing the charge valency of copper ions in copper tartrate. The peaks 2p_{3/2} and 2p_{1/2} observed at 934.65 eV and 953.73 eV respectively, in Figure 3 are assigned to the Cu²⁺ ions. The Cu 2p peak has a significantly split spin-orbit component with $\Delta = 19.08$ eV close to a value $\Delta = 19.08$ eV. A broad satellite peak is observed near 944.28 eV and These are strong Cu²⁺-satellites of 2P_{3/2} state 945.2 eV. It has been reported that strong satellite peaks appear in the XPS spectrum of transition-metal elements with unpaired electrons, but not for a closed-shell structure. In other words, Cu⁺ (d¹⁰) configuration does not show satellite peaks and Cu²⁺ (d⁹) shows such peaks. Therefore, the observed satellite peak at 945.2 eV is ascribed to Cu²⁺ ions [17,6]. Moreover, it has been reported that for transition metals, the absence of the satellite peaks is the fingerprint for elemental or diamagnetic lines. The occurrence of prominent satellites corresponds to the existence of the paramagnetic state [18,19]. This confirms the paramagnetic state of the copper tartrate crystal.

The oxygen 1s scan electron binding energy spectrum of copper tartrate is shown in Figure 4. The spectrum consists of the 1s peak at about 537.6 eV, which is ascribed to carbon with oxygen [19].

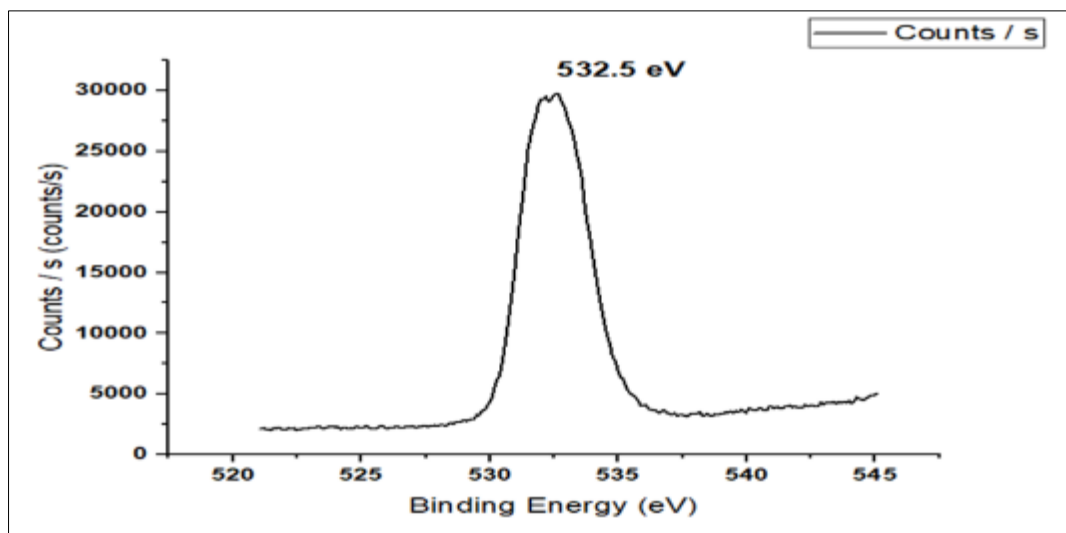


Figure 4 O1s Scan of Copper tartrate

The carbon 1s scan electron binding energy spectrum of copper tartrate is shown in Figure 5. It shows the 1s peak at about 292.3 eV, which is ascribed to carbonyl, that is, carbon with oxygen [20].

In chemical state O-C=O has B.E approximately 288.5 eV. 288.38 eV peak of B.E in C1S scan in Figure.5 shows this chemical state [21].

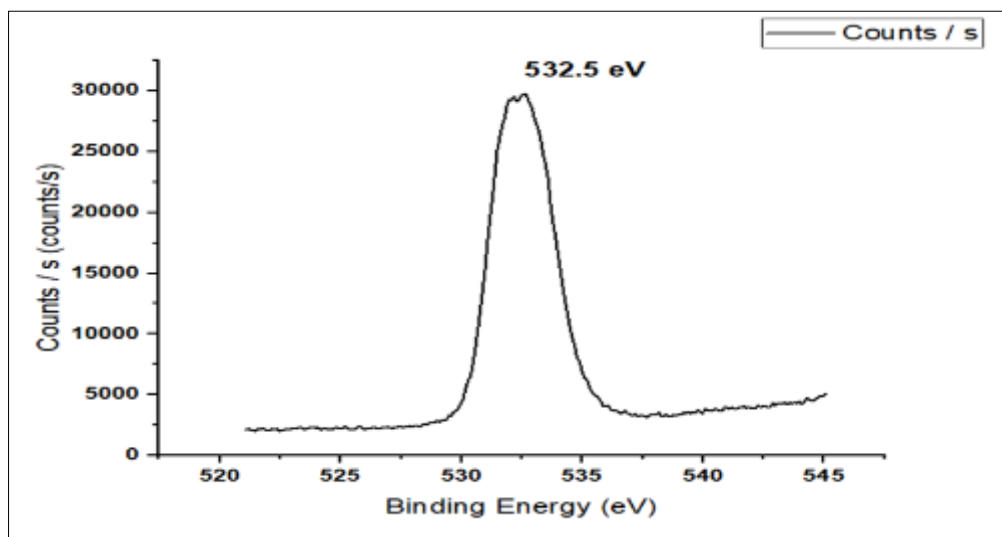


Figure 5 C1s scan of copper tartrate

The CuLM2 scan is performed for further study on copper oxidation states clearly.

Recorded XPS is shown in figure 6.

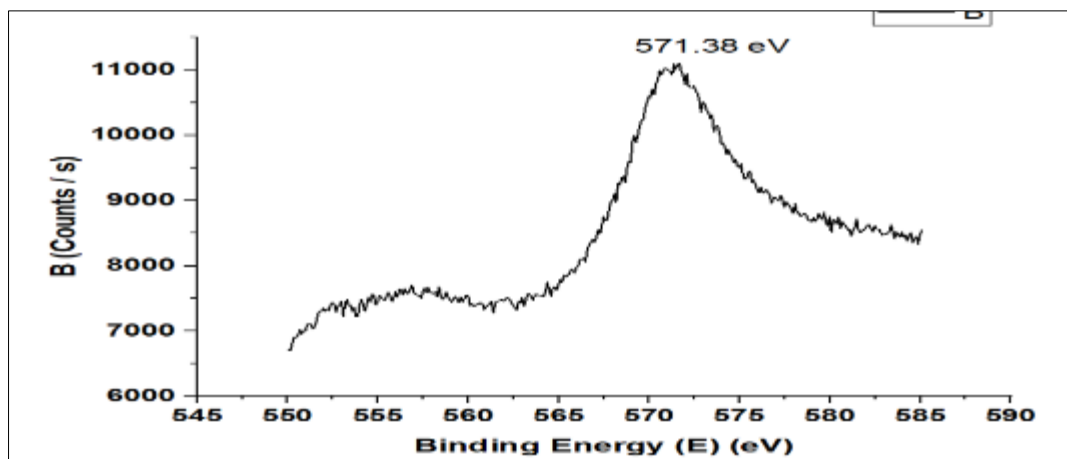


Figure 6 CuLM2 scan is assigned to Cu (OH)₂

CuLM2 scan is assigned to Cu (OH)₂ [17] as shown in figure 6.

2.4. Fourier-Transform Infrared Spectroscopy:

The FTIR spectrum was recorded using a Bruker ALPHA II model of spectrophotometer by the KBr pellet technique.

Kirschner and Kiesling studied the infrared spectrum of Cu (II) tartrates tri-hydrate. They found that tartrate was coordinated to Cu (II) through hydroxyl and 2-carboxylate groups [7].

FTIR is the fingerprint of material. FTIR analysis of single crystal pure Copper tartrate and Cadmium doped Copper tartrate is preliminary method of identifying a grown material. Functional group of a material, bonds in molecule of material are investigated. FTIR spectrum is recorded and analyzed. Wavenumbers in spectrum below 1500 cm^{-1} represent 'fingerprint Region' of molecule and wavenumbers above it represent 'Functional Group' region. Recorded FTIR spectra of single crystals of copper tartrate are as shown in figure 7 and Table 3 presents the observed absorption frequencies.

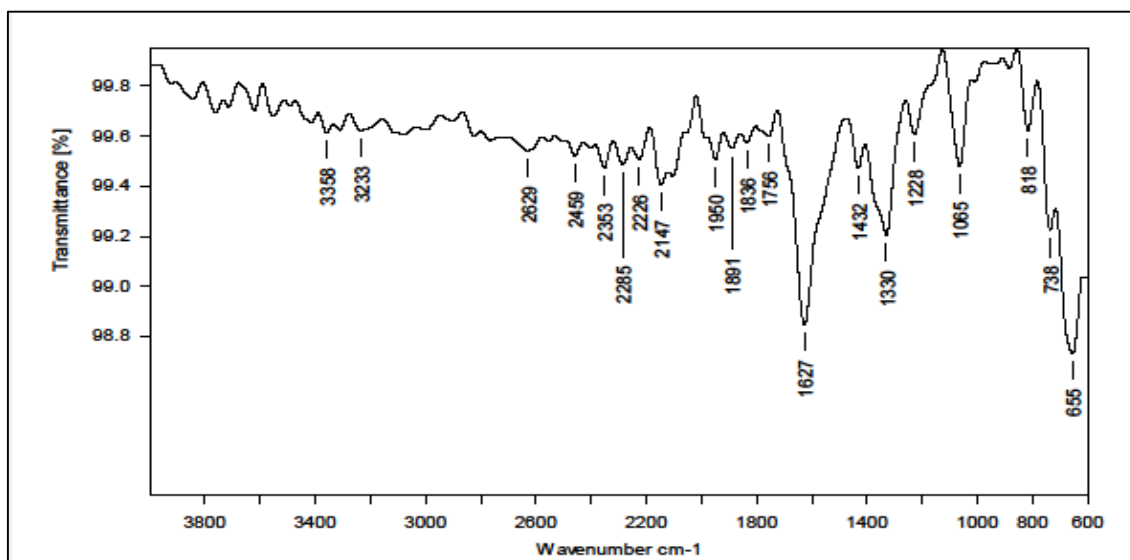


Figure 7 FTIR Analysis Curve of Copper tartrate

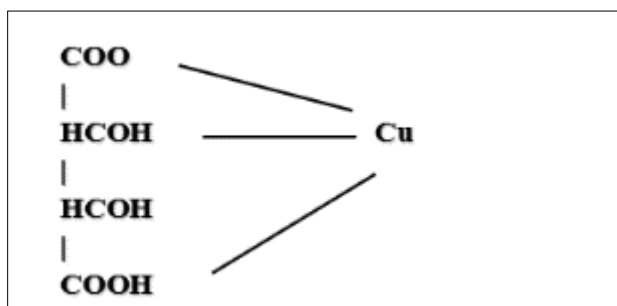
Table 3 Analysis of FTIR Spectra of $\text{CuC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$

Absorption in Wavenumber (cm^{-1})	Assignment
3233.2879,3416.1852,3551.3461,3384.16	OH-Stretching due to water bands
1626.7592	C=O due to oscillations of Carboxyl group
1227.9745,1330.3263	C-O Stretching vibration
1064.7854	C-H stretching vibration
1064.7854	O-H stretching out of plane vibration
737.5931,817.5367	Metal Oxygen bond stretching Vibrations (CuO)
1626.7592,1330.3263,1431.721,655.4870	Absorptions corresponding to Carboxyl group oscillations.

The FTIR spectrum shows that there are no wide water absorption band, but four small stretches at four frequencies are observed at wavenumbers $3233.2879 \text{ cm}^{-1}$, $3416.1852 \text{ cm}^{-1}$, $3551.3461 \text{ cm}^{-1}$, 3384.16 cm^{-1} [22].

In FTIR spectral analysis of copper tartrate crystals, carboxyl ion frequencies are noticed in the sample at wavenumber $1626.7592 \text{ cm}^{-1}$ which are assigned to C-H stretching vibration [7].

Proposed molecular structure of pure Copper tartrate for this research work is as shown in figure 8 below:

**Figure 8** Molecular Structure of pure Copper tartrate

3. Conclusion

Copper tartrate crystals were grown by the gel Growth method has prismatic morphology. They are semi-transparent. The orthorhombic unit cell volume is 933.835474 \AA^3 . FTIR confirmed the presence of the copper metal ion complex. XPS study has shown paramagnetic nature due to the presence of Cu^{2+} ion (d^9 state).

Compliance with ethical standards

Acknowledgments

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This is our original work for the degree of Doctor of Philosophy of Physics. This is self-funded work.

Disclosure of conflict of interest

All author declares that there is no conflict of interest.

Data Availability Statement

All datasets for this research are available upon request from the corresponding author.

Author Contributions

All authors contributed equally to the writing of this paper, and have read and approved the final draft.

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