

Synthesis and Structural Characterization of Copper Tartrate Crystals Grown in Silica Gel

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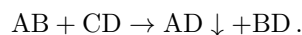
Abstract. Copper tartrate crystals were grown by the single diffusion method in silica gel by gel growth technique. Optimum conditions of crystal growth such as pH, specific gravity, aging period of gel, concentration of reactants in gels were determined by varying them. The unit cell of a grown crystal is characterized using powder X-ray diffraction. The Fourier transform infrared spectrum in the range 400–4000 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 Cu^{2+} ion.

KEY WORDS: Copper chloride, Sodium metasilicate, Tartaric acid, XPS.

1 Introduction

Wide variety of materials in single crystalline form have been synthesized in silica gel at ambient temperature using cost effective equipments [1–3]. Copper tartrate have been reported to be grown in silica gel [4–7] find applications related to electrical, magnetic, opto-electronic and medicinal properties. 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 happen, 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 [8]. The reaction mechanism can be shown as



In this study, crystalline product copper tartrate ($\text{CuC}_4\text{H}_4\text{O}_6$) is formed from diffusion of reactants copper chloride and tartronic acid in silica gel. The silica gel is obtained by the neutralization of the sodium metasilicate [9].

The basic principle behind sol-gel processing of silica based materials is the transformation Si-OH containing species to siloxane compounds by condensation reactions. From structural point of view this corresponds to connecting SiO_4 tetrahedra by corner sharing. To obtain a stable gel, the number of siloxane bonds (O-Si-O) has to be maximized and consequently the number of silanol (Si-OH groups) has to be minimized [10]. At around 3-4 pH, polymerization is initiated with formation of chain-like or open branch-like structures. This reaction repeats all over the solution to give a three-dimensional network of —Si—O links. As the polymerization process continues, water accumulates on top of the gel surface. Very high or very low pH values inhibit gelation. 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].

The gel is an ideal medium for diffusion reaction and it acts as a three-dimensional crucible holding the crystals in fixed positions without overlapping. 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/ml appear to represent a practical limit [14].

Under 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 Experimental

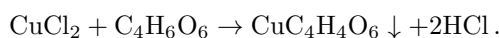
2.1 Materials and methods

Copper tartrate (CuC₄H₄O₆) crystals were grown by the gel growth method in silica gel by single diffusion technique. Copper chloride (CuCl₂) is used as an supernatant or outer reactant. Sodium metasilicate (Na₂SiO₃) is used to prepare silica gel by neutralization method by dissolving it into distilled water and tartaric acid (C₄H₆O₆). Tartaric acid is used as an inner reactant. All chemicals were of analytical grade.

2.1.1 Synthesis

Sodium metasilicate solution of 1M is prepared in deionized water. Specific gravity of silica gel was measured. For silica gel setting 1M sodium metasilicate solution was added to a 1M tartaric acid solution in a test tube until the pH value reached 4.0 and poured into in a round bottom cylindrical test tube of size 1.8 cm × 15 cm with flat circular bottom. Test tube is sealed for gelation. After the firm gel setting, 1M 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 colour 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.

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 × 3 mm × 1 mm 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 Table 1.



Figure 1. Crystal growth of copper tartrate in silica gel.

Table 1. Optimum conditions of Copper tartrate Crystal growth

Sr No	Specific parameter	Optimum value
1	Specific gravity of Sodium metasilicate	1.04 g/ml
2	pH of gel medium	4.00
3	Concentration of tartaric acid	1 M
4	Concentration of Copper Chloride	1 M
5	Gel Setting time	24-36 Hr
6	Growth period	1½ month
7	Gel aging	four days after gel setting

3 Results and Discussion

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

3.1 X-ray powder diffraction

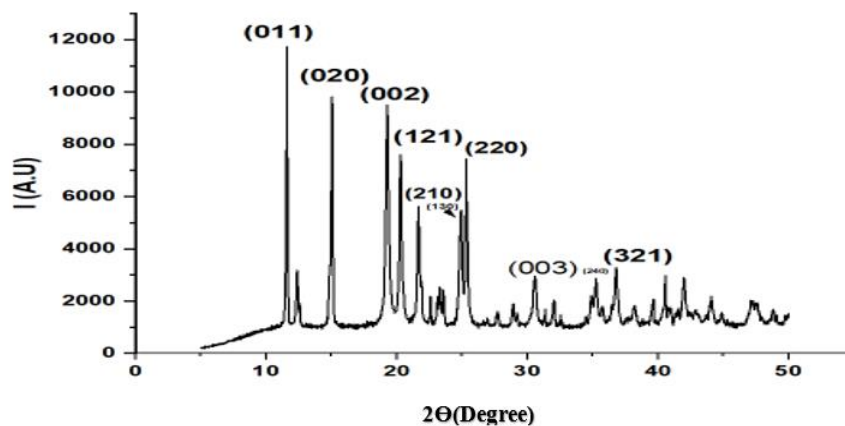


Figure 2. PXRD pattern peak data of copper tartrate.

The grown copper tartrate crystals were characterized by powder X-ray diffraction (PXRD). PXRD was performed by MeasSrv(B2)/250242 with copper $\text{K}\alpha$ radiation of wavelength 1.54060 Å. The PXRD has recorded reflections from angle (2θ) 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 $a = 8.6716637$ Å, $b = 11.76998$ Å, $c = 9.20782$ Å and $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$, which are in agreement with the reported [6, 7] and intensities are matched COD ID 7023997 [16]. The volume of unit cell of copper tartrate crystal is 933.835474 Å³ with space group $\text{P}2_12_12_1$.

3.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) by $\text{K}\alpha+$ made at M/s Thermo Fisher Scientific Instruments. The copper 2p scan electron binding energy spectrum of copper tartrate is shown in Figure 3.

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 Cu^{2+} 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 Cu^{2+} satellites of 2P_{3/2} state 945.2 eV. It has been reported that strong

Table 2. PXRD Data of copper tartrate

Obs_Max ($2\theta^\circ$)	d Å Obs_Max	Indices of plane (h, k, l)
11.5870	7.63119	011
12.3740	7.14750	110
15.0423	5.88499	020
19.263	4.603910	002
20.285	4.374290	121
21.655	4.100570	210
24.901	3.572950	130
25.316	3.152000	220
30.571	2.921880	003
36.787	2.441210	321
35.242	2.544595	240

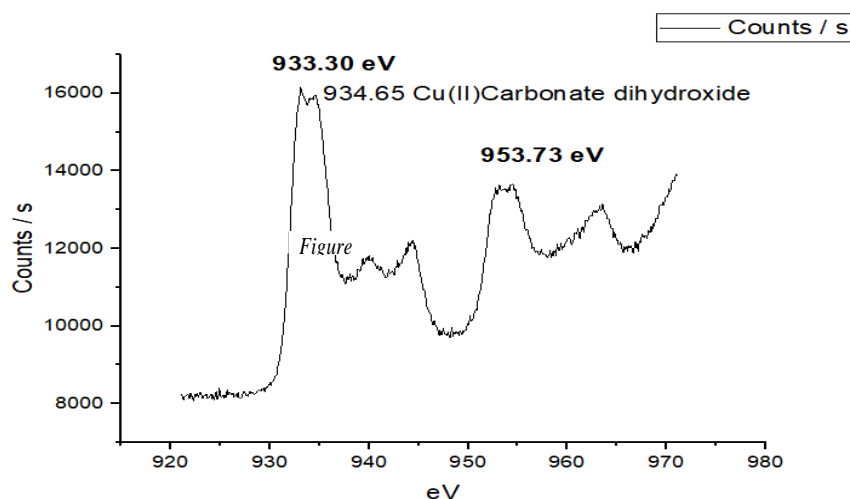


Figure 3. Cu2p scan of copper tartrate single crystal.

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^+ (d^{10}) configuration does not show satellite peaks and Cu^{2+} (d^9) shows such peaks. Therefore, the observed satellite peak at 945.2 eV is ascribed to Cu^{2+} ions [6, 17]. 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].

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. The peak at 288.38 eV of B.E in C1S scan in Figure 5 shows this chemical state [21].

The Cu LM2 scan is performed for further study on copper oxidation states

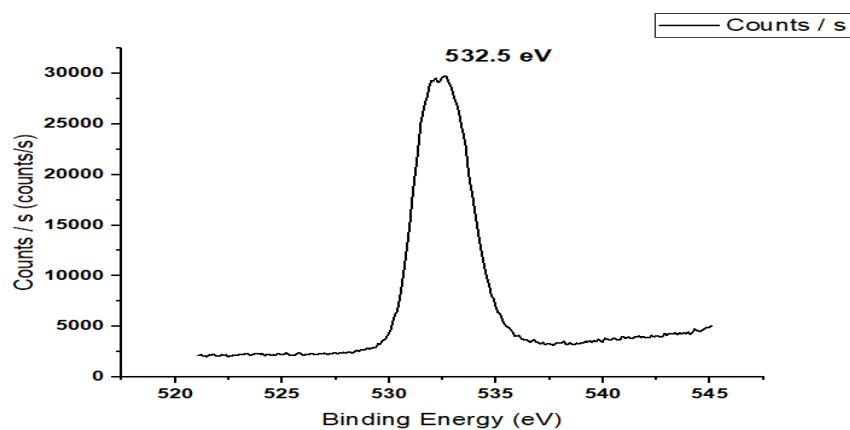


Figure 4. O1s scan of copper tartrate

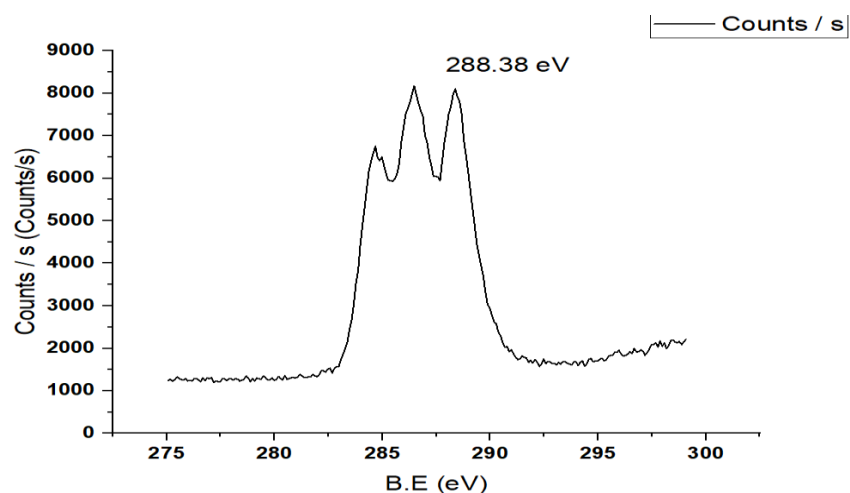


Figure 5. C1s scan of copper tartrate.

clearly. Recorded XPS is shown in Figure 6.

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

3.3 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 trihydrate. They found that tartrate was coordinated to Cu (II) through hydroxyl and 2-carboxylate groups [7].

FTIR is the fingerprint of materials. 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 analysed. 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.

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 cm⁻¹, 3416.1852 cm⁻¹, 3551.3461 cm⁻¹, 3384.16 cm⁻¹. Less than one water molecule may be present in the crystal from TGA-DSC analysis performed in this study. In FTIR spectral analysis of copper tartrate crystals, carboxyl ion frequencies are noticed in the sample at wavenumber 1626.7592 cm⁻¹.

Proposed molecular structure of pure copper tartrate for this research work is as

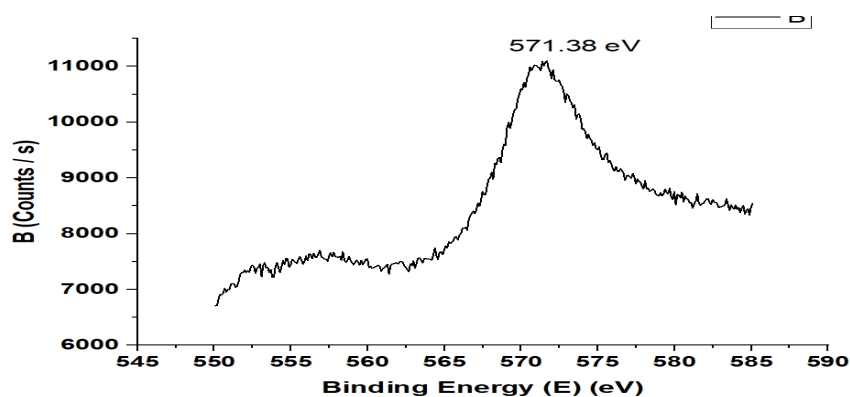


Figure 6. Cu LM2 scan of copper tartrate.

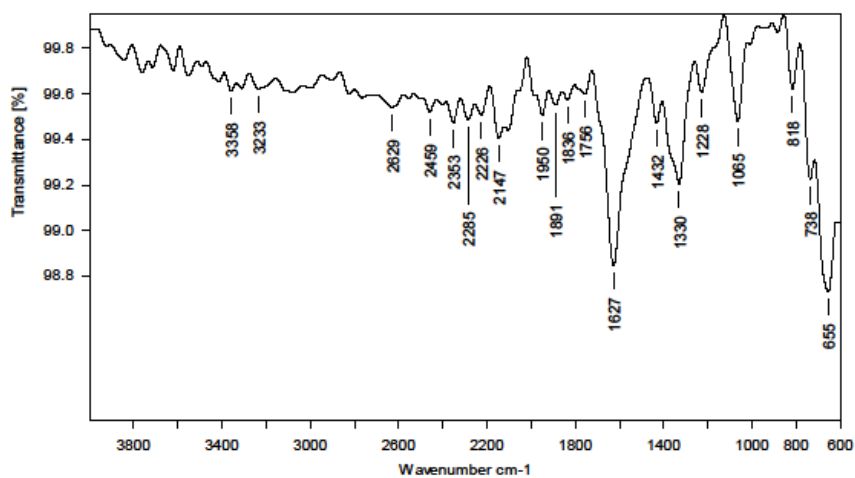


Figure 7. FTIR analysis curve of copper tartrate.

Table 3. Analysis of FTIR spectra of copper tartrate

Absorption in wavenumber cm^{-1}	Assignment [7,22]
3233.2879, 3416.1852, 3551.3461, 3384.16	OH-stretching due to water bands [22]
1626.7592	C=O due to oscillations of carboxyl group [22]
1227.9745, 1330.3263	C-O stretching vibration [7]
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

shown in Figure 8.

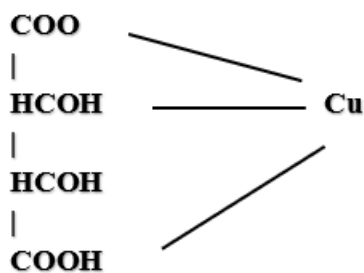


Figure 8. Molecular structure of pure copper tartrate.

4 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 and the presence of Cu^{2+} ion (d^9 state).

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