

Electro-optical and thermal characterization of copper tartrate crystals grown in silica gel

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Abstract

Copper Tartrate crystals were grown by Gel Growth technique by single diffusion. Silica gel of Optimum specific gravity was set with tartaric acid at optimum pH and aging period. Band gap of copper tartrate crystal is determined using UV-Visible spectroscopy to be 5.24 eV. In PL spectra broad peak is observed at nearly 367.44186 nm in the range 287 nm to 458 nm along with the sharp, intense transmission maxima peak at wavelength nearly 505.03876 nm which is characteristic of a material composition and electronic band structure. This shows the transparency in UV-visible region and material is a filter in this range. TGA analysis concluded that Copper tartrate has one half water molecule as crystalline water and is stable up to 85.02 °C. DSC analysis assigns the temperature value 314.5 °C as melting point and apparent enthalpy of fusion determined is 10.18 mW.

Keywords: Silica gel; Chemical reaction; TGA; DSC; UV; PL

1. Introduction

Scientific bases of gel methods for low solubility crystals have been established by Henisch at the beginning of the seventies. Later on, these methods were applied to soluble materials having a low molecular weight. More recently, some attempts have been made to extend gel techniques to high-molecular-weight substances like organic and protein crystals [1].

Liesegang's structures were (quite properly) called rings, because they were first observed in that form, i.e. as concentric deposits in a plane. Later they were more often grown in test tubes, and were therefore disks, often they consisted of apparently amorphous material but, in due course, the achievement of microcrystalline reaction products came to be seen as desirable, because of the ease with which they could be identified by means of x-ray photographs. Larger crystals, several min size, were occasionally obtained, but not systematically not systematically looked for.

Wide variety of materials in single crystalline form have been synthesized in Silica gel at ambient temperature using cost effective equipment [2,3,4].

Copper tartrate have been reported to be grown in silica gel [5,6,7,8] 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 the 'single diffusion' and by 'Chemical Reaction Method'¹[2]

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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 (Tartaric acid) inside the gel, and a solution of salt B (Copper Chloride) is poured onto the top of the gel. When the diffusion of B throughout the gel is happening, the crystallization process of compound C (Copper tartrate) takes place inside the gel network; this C compound is not soluble in water if the gel is a hydrogel [9].

The silica gel is obtained by the neutralization of the sodium metasilicate.

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. It is a chemically inert, transparent system for growing good-quality crystals. It is possible to observe the entire growth process and the grown crystals can be harvested easily. Gel method allows effective control over factors such as density, concentration, and pH, Nucleation, Subsequent crystal growth.

The habit of a crystal is mainly controlled by kinetic factors. The habit is defined by the relative rates of crystalline growth in different directions; the faster the growth in a given direction, the smaller the face developed perpendicular to it. The environmental conditions in which the crystallization takes place (solvent choice, temperature, pressure, etc.) have a great influence on the crystal habit. To a very careful observation of tartrate salt crystals, Pasteur was able to see the presence of minor faces that had been overlooked by others. These faces showed that the morphology and structure of the crystals were chiral respectively. It is worth remembering that any optically pure chiral compound must crystallize in a chiral point group [10].

Experimenters have realized that solutions with densities in the range of 1.03–1.06 g/ml yield satisfactory results. Silica gel of specific gravity 1.04 g/ml at pH value of 4 with tartaric acid has yielded optimum crystal growth.

In this study concentration of outer reactant is varied to study effect of its concentration and effect pH of Silica gel on the habit of grown of crystals. Thermal characterization techniques are used to study stability of material and its decomposition on heating.

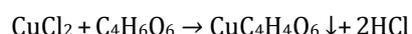
2. Materials and Methods

Copper tartrate ($\text{CuC}_4\text{H}_4\text{O}_6$) crystals were grown by the gel growth method in silica gel by single diffusion technique. Copper Chloride (CuCl_2) is used as a supernatant or outer reactant. Sodium metasilicate (Na_2SiO_3) is used to prepare silica gel by neutralization method by dissolving it into distilled water. Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) is used as an inner reactant or inner reactant. All chemicals were of analytical grade. 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 to 4.0. After a firm gel setting, gel was allowed to age for the period of 1 day to 12 days. It was observed that aging of 3 days is better for optimum crystal growth. 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. Next day, pure copper tartrate crystals of bluish color were seen growing. Within 30–45 days crystal growth is complete and the gel structure holding crystals seems sinking to bottom of the test tube. In this work 5ml, 10ml, 20 ml CuCl_2 solution was used in three test tubes. Effect of variation of outer reactant is observed at constant aging period of 12 days.

Silica gel is a 3D skeleton of Silicic acid. It is inert -Si-O-Si network. Within this crucible crystal growth takes place. Within its pore nucleation takes place. Diffusion of copper ions and tartrate ions lead to mass transport and react to produce bluish copper tartrate crystals. Habit of crystals is tabular.

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



Observations:

Observations are illustrated in the table1 below.

Table 1 Variation of outer reactant and morphology in Crystal Growth of $CuC_4H_4O_6$

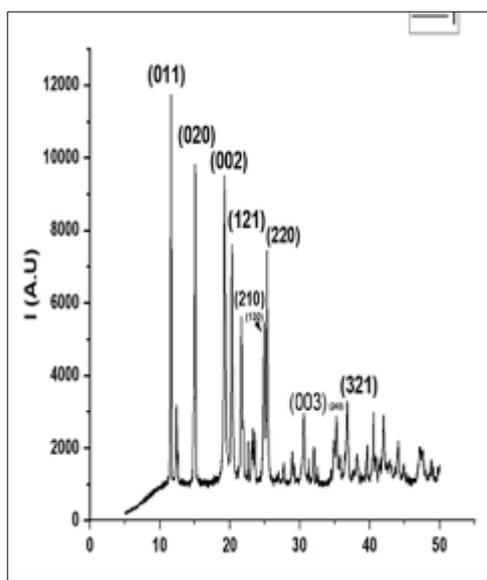
Sr No	Volume of outer reactant CuCl2	Size, Morphology
1	5 ml,1M	Tabular, Opaque,1 mm x1mm x0.1 mm size
2	20ml,1M	Irregular -rock type, Opaque,6mm in length
3	10 ml,1M	Irregular-rock type, Opaque,5mm in length

3. Characterizations and Results with discussion

Dimensions of a unit cell of the grown copper tartrate ($CuC_4H_4O_6$) are determined from Powder X-Ray Diffraction (PXRD) data. Ultra-Violet Visible (UV-Vis) spectroscopy has been used to determine 'Energy Band Gap' and Photoluminescence (P. L) Spectroscopy has been used to determine 'Transparency' range or color of copper tartrate single crystals. Thermal studies like Thermogravimetric Analysis (T.G.A) and Differential Scanning calorimetry (D.S.C) is used to study thermal decomposition, constituents, melting point and stability of $uC_4H_4O_6$.

3.1. X-ray Powder Diffraction

The powder XRD pattern of copper tartrate is shown in Figure 1. The peaks are indexed by the method of least- squares fit from the XRD data as illustrated in the table .2. The crystal is found to be crystallized in the orthorhombic structure with lattice parameters $a = 8.6716637 \text{ \AA}$, $b = 11.76998 \text{ \AA}$, $c = 9.20782 \text{ \AA}$ and $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$, which are in agreement with the reported values [7,8] and matched with The JCPDS card number is 01-0158.COD ID 7023997.Calculated Unit cell dimensions of crystal using recorded data are nearly in agreement with [7,8].

**Figure 1** PXRD Data of Copper tartrate**Table 2** PXRD Diffraction Data of Copper tartrate

Sr. No	$2\theta^\circ$	$d \text{ (\AA)}$	Indices of d Plane (h, k, l)
1	11.587	7.63119	011
2	12.374 0	7.14750	110
3	15.042 0	5.88499	020
4	19.263 0	4.60391	002
5	20.285 0	4.37429	121

6	21.655 0	4.10057	210
7	24.901 0	3.57295	130
9	25.316 0	3.1520	220
10	30.571 0	2.92188	003
11	36.787 0	2.44121	321
12	35.242 0	2.54459	240

3.2. Electro-Optical Characterization

Author has termed determination of optical transparency (Color) and Energy band gap as 'Electro-Optical characterization'. UV-Visible spectroscopy and Photoluminescence spectroscopy is used to determine these characteristics.

3.3. UV-Vis Spectroscopy

The absorbance data of copper tartrate is collected from wavelengths 200 nm-800 nm on UV-Vis 1000 Spectrophotometer at H.R. Patel Pharmacy, Nano lab, Shirpur.

The UV-Vis absorbance spectra collected in the wavelength range 200 nm- 800 nm is as shown in the figure 2 below.

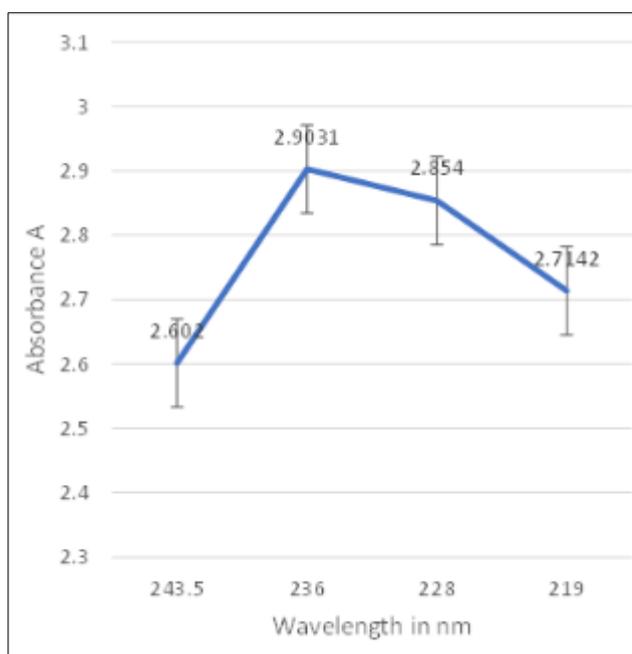


Figure 2 UV-Vis Spectrum of $\text{CuC}_4\text{H}_4\text{O}_6$

From the data of UV-Vis Spectrum as shown in Figure 3, the maximum absorption has occurred at wavelength (λ_{max}) 236 nm. The band gap of copper tartrate crystal can be calculated as,

$$E_g = \frac{hc}{\lambda_{max}} \text{ in eV} = \frac{1240}{236} \text{ eV} = 5.243729 \text{ eV}$$

This value is close to the reported value 5.48 eV [2] to [5]. The energy band gap of grown copper tartrate is 5.24 eV. The high absorption in the ultra-violet region at about 236 nm makes the material is good for UV absorbers/filters and the wide transmission in the entire visible region enables it suitable candidate for optoelectronic applications.

3.4. Photoluminescence spectroscopy (PL)

For powder sample, emission data is collected from wavelength 275 nm to 800 nm on instrument Fluoromax_PLUSC R928P at NCL Pune as shown in figure 3. Broad transmission is observed from 275 nm to 800 nm with a peak at 367.44186 nm. The sharp transmission maxima is observed at wavelength 505.03876 nm. These transmission peaks are in the UV-Visible range of electromagnetic spectrum. They are characteristic of a material composition and electronic band structure. Broad Peak is observed at near 367.44186 nm in the range 287 nm to 458 nm along with the sharp, intense transmission maxima peak at wavelength nearly 505.03876 nm which is close to value 508.6 nm reported [5] and small intensity peak at 765 nm close to 766.8 nm the reported value [7].

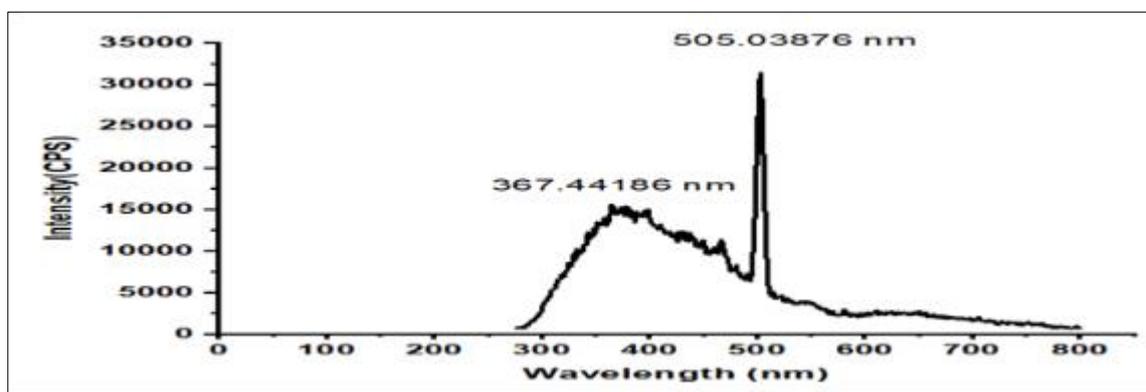


Figure 3 Photoluminescence Spectrum of $CuC_4H_4O_6$

3.5. Thermal Characterization

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are thermal characterizations to study thermal decomposition, constituents and stability of $CuC_4H_4O_6$ respectively.

3.5.1. TGA

TGA is conducted on instrument known as thermogravimetric analyzer 'TGA 55 TA Instruments, Denmark' with Equilibrate 30.00 °C; Ramp 20.00 °C/min to 800.00 °C at KBCNMU, Jalgaon. The mass of sample is continuously measured with temperature over time. The recorded thermogram provide us information about physical and chemical changes or properties of a material. It helps us investigation of stepwise decomposition of grown single crystal and stability of it.

The sample loose or gain weight on heating due to different processes on heating. Thermogram of Pure Copper Tartrate ($CuC_4H_4O_6$) single Crystal is the graphical representation of percentage weight loss during decomposition at varying temperatures due to heating or cooling under controlled programming. Thermogram obtained in TGA is as shown in figure 4.

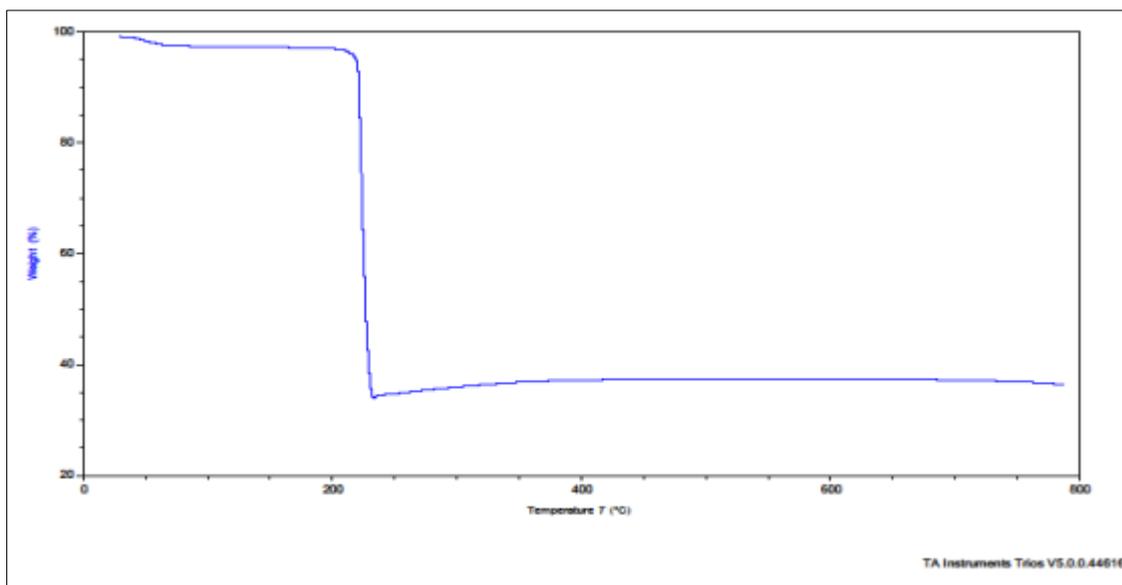
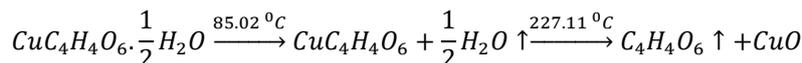


Figure 4 Thermogram of $\text{CuC}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$

Recorded thermogram shown in figure 4 is analyzed and found close to the reported [8] as below in table 3:

TGA analysis curve in figure 4 indicate loss of nearly 4% mass resembling with mass of $\frac{1}{2}\text{H}_2\text{O}$ during decomposition at 85.02 °C followed by rapid decomposition into CuO at 220. 70 °C. A small dip is Observed at 227.12 °C followed by stable state. One may conclude that it is due to decomposition of anhydrous Copper tartrate into $\text{Cu} + \frac{1}{2}\text{O}$ and subsequent picking up of Oxygen from air to give residual CuO. Hence, we may show the decomposition of pure Copper Tartrate as below:



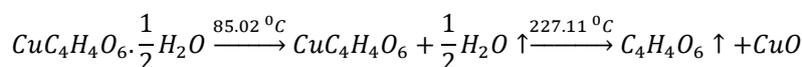
One may conclude that Copper tartrate is stable up to 85.02 °C.

Table 3 Decomposition Analysis of TGA Curve Recorded at Ramp 20 °C/min to 800 °C

Sample	Temperature (°C)	Decomposition of single crystals	Theoretical Weight of present sample (%)	Observed Weight (%)
Pure Copper Tartrate	Room Temperature	$\text{CuC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$	100%	100%
	85.02 °C – 98.06 °C	$\text{CuC}_4\text{H}_4\text{O}_6$	95.92	97.396
	227.12 °C	CuO	36.056	37.743

TGA analysis of samples shows loss of 0.5 water molecule and hence the presence of 0.5 H_2O molecule in a Crystal.

From TGA analysis the decomposition of Pure Copper Tartrate can be shown by following reaction:



It is concluded that single crystal material of pure Copper tartrate is stable up to 85.02 °C.

3.5.2. Differential Scanning Calorimetry (DSC)

A DSC analyzer records the energy changes which occurs as a sample material is heated, cooled or held isothermally, together with the temperature at which these changes occur. In the differential thermal analysis, the energy difference inputs between a sample and a reference material is measured as a function of temperature when the substance and reference material are subjected to a controlled temperature program. The graph of heat flow on Y-axis is plotted versus temperature at a fix rate of change of temperature on the X-axis shows the output of DSC. In DSC analysis, form the energy changes one can find and measure the transitions that occur in the sample material and can note the temperature where they occur.

DSC is a calorimetric method, in which DSC curve was analyzed to study stability of material on heating and its decomposition.

DSC was performed on the instrument 'Hitachi DSC 7020' at KBCNMU, Jalgaon.

In this method, aluminum pan is used to put the weighed sample powder. The surrounding medium was air. The sample was heated at the rate of 20 °C/min up to 350 °C. The change in energy in mw was recorded as a function of temperature, which provides the information of exothermic or endothermic peaks at the time of dehydration or decomposition. Probably the common use of DSC is in fingerprinting n which simple or complex materials can be compared for identification using measurements of peak positions, sizes or shapes.

DSC analysis of the grown crystals was recorded between 0.210371047 °C to 350 °C in the nitrogen atmosphere and the heating rate was maintained at 20 °C /min. These methods are commonly used in chemical analysis and for obtaining thermodynamic data.

In the DSC curve, we can observe three endothermic peaks at 96.7 °C, 277.4 °C, 314.5 °C and one exothermic peak at 286.2 °C. The DSC data collected from the DSC curve is shown in Fig.5 and illustrated in the table 4 below:

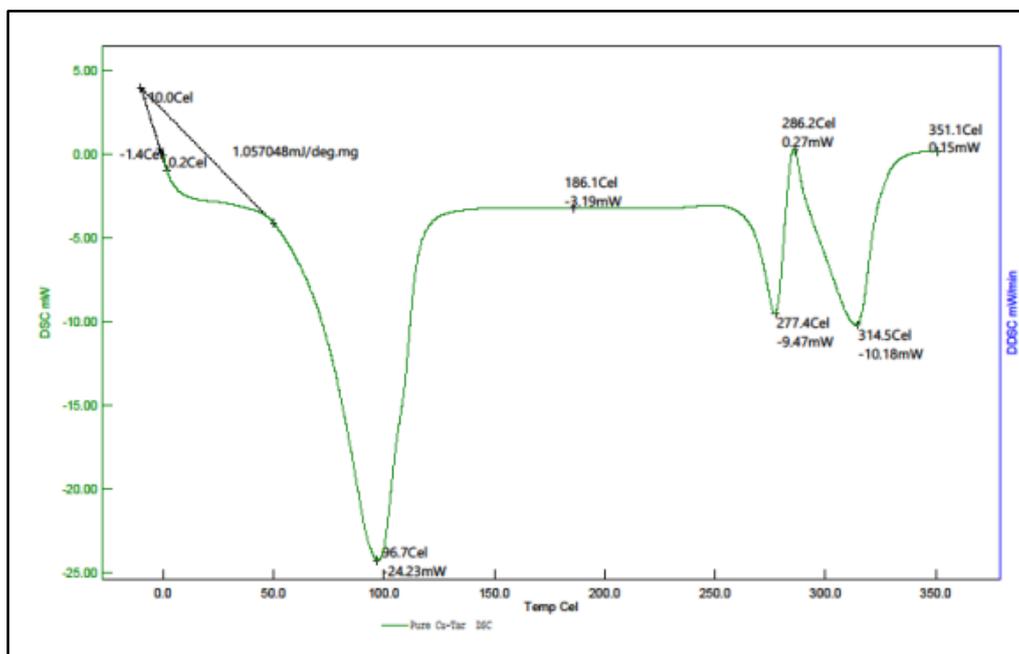


Figure 5 1DSC Analysis Curve of Pure Copper Tartrate

Table 4 DSC Curve Analysis Of $\text{CuC}_4\text{H}_4\text{O}_6$ to [11]

Sample	Peaks	Temperature (°C)	Remark
$\text{CuC}_4\text{H}_4\text{O}_6 \cdot n\text{H}_2\text{O}$	Endothermic	96.7	Energy absorbed during a loss of H_2O
	Exothermic	286.2	Energy evolved during a loss of CO_2
		351.1	Energy evolved during a loss of $\text{CH}_4 + \text{CO}$

The endothermic peak at 96.7 °C is due to the dehydration of water molecules while heating. This endothermic peak observed in the DSC curve reveals that the heat is absorbed during the reaction. The temperature 96.7 °C represents the equilibrium temperature. In DSC analysis system has to maintain the constant heat of both sample pan and reference pan. In endothermic reaction heat will be absorbed during the reaction. Hence heat of the sample decreases and to maintain same heat of sample and reference heat will be provided by system. This provided heat shown by peak value of endothermic peak.

When a water molecule absorbs heat energy to overcome the vapor pressure it will escape and enter the surrounding. When evaporation occurs, the heat energy removed from the material. Therefore, heat of sample decreases. To maintain the same heat of sample and reference, system provides the heat to sample. This heat is shown by the peak value of endothermic peak at 96.7 °C.

The exothermic peak at 286.2 °C is due to the decomposition of copper tartrate compound and this peak may correspond to the second stage of TGA decomposition. This exothermic peak observed in the DSC curve corresponding to the weight loss of CuO molecules in the TGA curve. In order to decomposition into the Carboxylate ion and CuO some old bonds are break and new bonds are formed to make $\text{C}_4\text{H}_4\text{O}_6^{2-}$ molecule. In the formation of new bond energy were released. Hence, the heat of sample is increased. To maintain the same heat of sample and reference system absorbs the heat from sample. This heat is shown by the peak value of exothermic peak at 286.2 °C.

Endothermic peaks at 61.0 °C, 261.0 °C are assigned to decomposition of tartrate diradical to $\text{C}_2\text{H}_2\text{O}_3$ at 271 °C and further decomposition of $\text{C}_2\text{H}_2\text{O}_3$ to formaldehyde and CO_2 at 282.1 °C, decomposition of $\text{C}_4\text{H}_4\text{O}_6^{2-}$ to $\text{C}_4\text{H}_4\text{O}_6$ & O_2 at 306.3 °C, decomposition of $\text{C}_4\text{H}_4\text{O}_4$ to CH_2 , H_2O , CO , C_2H_2 and CH_2O .

Exothermic peak at 294.6 °C is assigned to conversion of $\text{C}_4\text{H}_4\text{O}_6^{2-}$ into an isomeride with a hexatomic ring & Oxidation of Cu Species [11].

Temperature 314.5 °C may be assigned to apparent melting.

Apparent Enthalpy of Fusion determined is 10.18 mW.

4. Conclusion

The crystals of tabular habit are grown by gel growth technique at room temperature. UV-Vis spectroscopy gives band gap value of 5.24 eV as band gap of copper tartrate crystalline material. In PL spectra broad peak is observed at nearly 367.44186 nm in the range 287 nm to 458 nm along with the sharp, intense transmission maxima peak at wavelength nearly 505.03876 nm They are characteristic of a material composition and electronic band structure. This shows the transparency in UV -visible region and a filter in this range. TGA analysis concludes that Copper tartrate has one half water molecule as crystalline water and is stable up to 85.02 °C. DSC analysis assigns the temperature value 314.5 °C as melting point and apparent enthalpy of fusion determined is 10.18 mW.

Compliance with ethical standards

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Disclosure of conflict of interest

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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