

(RESEARCH ARTICLE)



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

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Abstract

Cadmium doped 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 for crystal growth. Band gap of cadmium doped copper tartrate crystal is determined using Ultraviolet-Visible Spectroscopy is 5.780 eV. Blue Color of cadmium Copper tartrate crystal and transparency is confirmed using Photoluminescence spectroscopy. Emission originates from Cu^{2+} vacancy-related defects or their complexes. Dimensions of crystals are found from Powder X-Ray Diffraction data. The edge lengths of unit cell calculated from indexing of PXRD data are, $a = 5.47 \text{ \AA}$, $b = 11.76 \text{ \AA}$, $c = 9.20 \text{ \AA}$ and volume of unit cell is, 621.02208 \AA^3 .

Keywords: Cadmium Chloride; Copper Chloride; Tartaric acid; Sodium Meta Silicate; PL; UV-Vis; PXRD

1. Introduction

Wide variety of materials in single crystalline form have been synthesized Silica in gel at ambient temperature using cost effective equipment [1,2,3].

Copper tartrate have been reported to be grown in silica gel [4] find applications related to electrical, magnetic, Opto-electronic and medicinal properties. Also, several doped copper tartrate crystals were grown by the gel technique, for example, sodium modified, iron doped and manganese doped copper tartrate crystals and cadmium doped copper tartrate [4] CCT crystals are transparent to visible light. This allows them to be used for window applications, where the crystalline perfection and optical transparency is essential. As crystals behave as insulators and UV-Vis filter find suitable for the fabrication of materials for opto-electronic devices. They can be used to develop copper clad laminates in PCBs and also various application of in the electronic industries [5].

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]. 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 [6].

The silica gel is obtained by the neutralization of the sodium metasilicate [7].

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The basic principle behind sol-gel processing of silica-based materials is the transformation of Si-OH containing species to Siloxane compounds by condensation reactions. From structural point of view this corresponds to connecting SiO₄ 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 [8].

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 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 [9,10].

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 ease with which 'over doping' can occur may have something to do with the yielding nature of the gel which, in a sense, serves as a three-dimensional quartz 'crucible' but exerts only very small constraining forces on the growing crystal. Since the silica network is chemically stable, it does not itself contaminate the growing crystals to any appreciable extent [2,11].

Most crystallized inorganic materials are ionic. This means that dissociation reactions, ionic interactions, and solution acidity (pH) determine the solubility of inorganic compounds in aqueous solutions. Experiments suggest that a solvent in which the compound has a solubility between 10% and 60% at a given temperature is suitable for crystal growth. These growth rates from solutions fall in the range of 0.1–1 mm/day [12].

Concentration programming has been successfully applied to the control of nucleation and growth to yield cuprous tartrate crystals of large size up to 3 mm or more than without concentration programming 1 mm and higher degree of perfection than those produced without concentration programming [9,3].

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

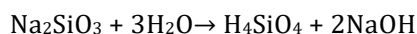
2. Material and methods

Cadmium doped Copper tartrate ($Cd_xCu_{(1-x)}C_4H_4O_6$) crystals were grown by the gel growth method in silica gel by single diffusion technique. 1M Copper Chloride ($CuCl_2$) is mixed with 0.5M $CdCl_2$ used poured as a supernatant or outer reactant over the set gel. Sodium metasilicate (Na_2SiO_3) is used to prepare silica gel by neutralization method by dissolving it into distilled water. Tartaric acid ($C_4H_6O_6$) 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 4.0. After a firm gel setting, Cadmium doped Copper tartrate ($Cd_xCu_{(1-x)}C_4H_4O_6$) crystals were grown by the gel growth method in silica gel by single diffusion technique. 1M Copper Chloride ($CuCl_2$) is mixed with 0.5M $CdCl_2$ used poured as a supernatant or outer reactant over the set 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 (Fig. 1) at optimum conditions illustrated in table 1. Within 30-45 days crystal growth is complete and gel structure holding crystals seems sinking to bottom of the test tube.

The silica gel is obtained by the neutralization of the sodium metasilicate with tartaric acid. This reaction is indicated as follows:

The synthetic pathways to obtain hydrogels from the neutralization of sodium metasilicate (SS) solution are as follows:



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.

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

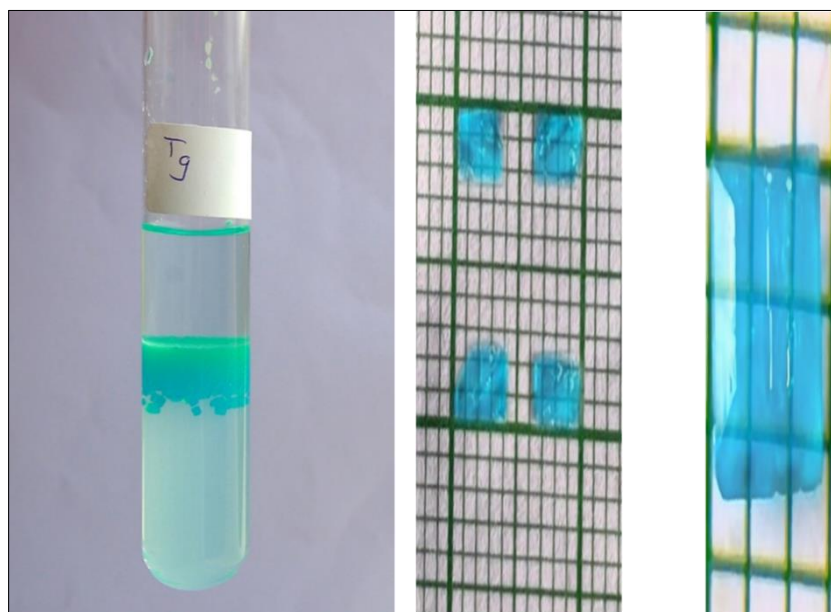
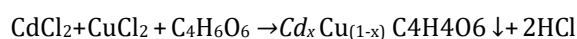


Figure 1 a) Crystal Growth of $\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$ b) and c) Crystals Grown

Table 1 Optimum Conditions for Crystal Growth of $\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$

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' mixed with 0.5 M 'Copper chloride'	1M CuCl_2 + 0.5 M CdCl_2
5	Gel setting time	24 Hr -36 Hr
6	Growth period	1½ month
7	Diffusion method	Single diffusion
8	Gel Aging	4 days after Gel Setting

3. Results and discussion

3.1. Powder X-ray Diffraction (PXRD)

The PXRD data of Cd doped Copper tartrate is collected in the form of 'intensity(I)' and '2θ'. Some intensity peaks of recorded PXRD match with the JCPDS card number is 01-0158.COD ID 7023997 of copper tartrate and the corresponding observed maximum 'd' values from PXRD data are used to calculate dimensions of unit cell of Cd doped copper tartrate crystal. The dimensions of unit cell are;

- $a = 5.47^{\circ}\text{A}$
- $b = 11.76^{\circ}\text{A}$
- $c = 9.20^{\circ}\text{A}$
- $V = 621.02208^{\circ}\text{A}^3$

Doping of Cd in Copper tartrate has affected dimension such as edge length 'a'. 'a' is 8.67°A for author's reported value of copper tartrate crystal's unit cell edge length. Edge lengths of unit cell of crystal b, c are nearly same as in the reported values [13],[4] and JCPDS card number is 01-0158.COD ID 7023997.

The intensity peaks match with Copper tartrate. Other peaks in Copper tartrate are absent. One may conclude that Cd is doped or occupy lattice of Copper tartrate.

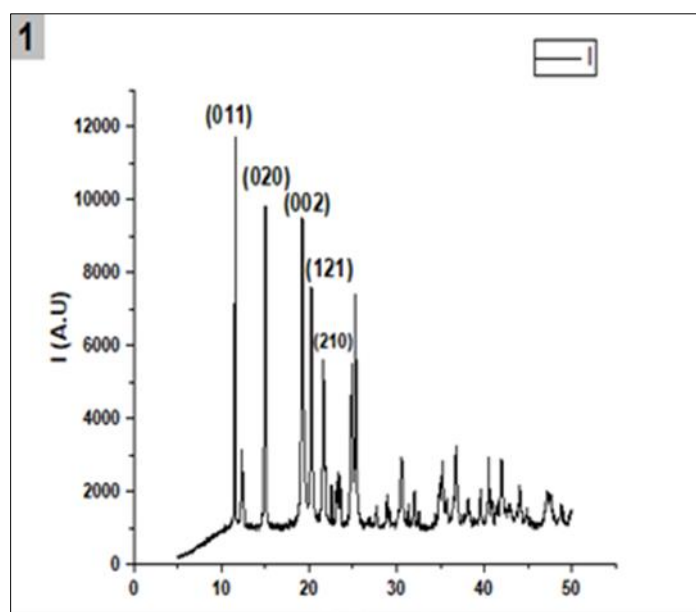


Figure 2 Powder X-Ray diffraction of $\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$ crystal

Table 2 PXRD Data for Cd doped Copper tartrate crystals

Obs.Max 2θ(°)	d(Obs.Max in °A)	Indexing d to (h,k,l) value
11.590	7.62927	(0,1,1)
15.045	5.88381	(0,2,0)
19.279	4.60033	(0,0,2)
20.311	4.36877	(1,2,1)
21.893	4.05646	(2,1,0)
25.335	3.51268	(2,2,0)

3.2. Electro-Optical Characterization

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

3.2.1. Ultra-Violet (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-Visible spectrum gives very important information of the absorption of U. V and visible light, which involve the transition of electrons in σ and π bond from the ground level to higher energy level. The compounds with CO group absorb light in this range. The UV-Visible spectrum gives information about the transparency window which is very essential in optoelectronic applications.

The UV-Vis absorbance spectra collected in the wavelength range 200 nm- 800 nm is as shown in the figure 3 below:

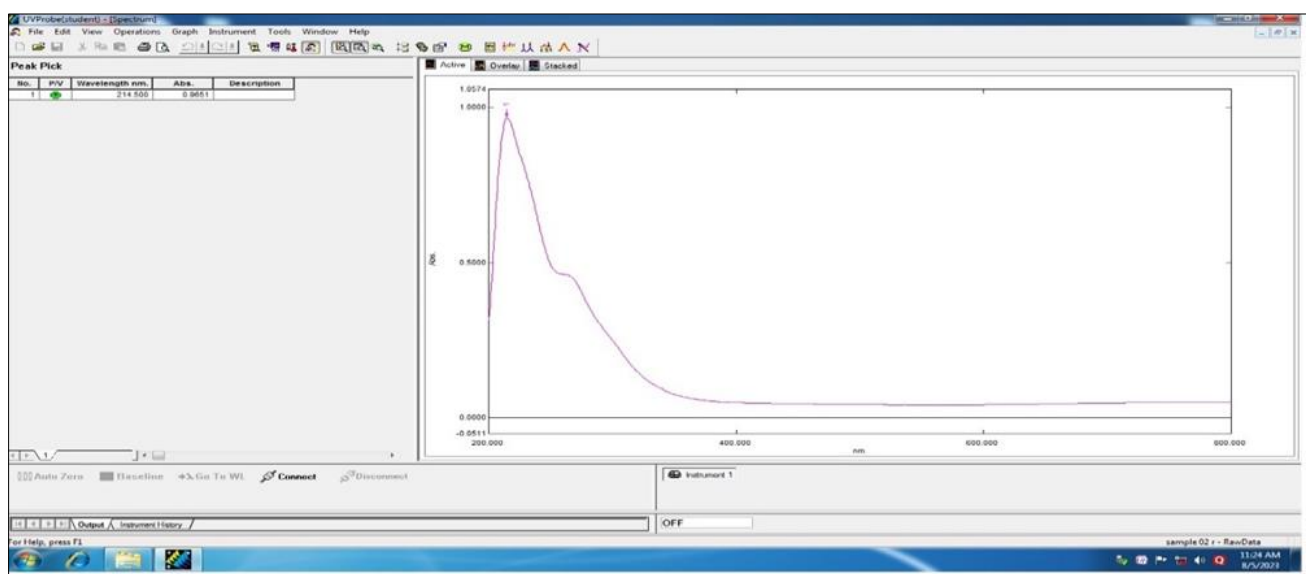


Figure 3 UV-Vis Spectrum of $Cd_xCu_{(1-x)}C_4H_4O_6$ crystal

From the data of UV-Vis Spectrum as shown in Figure 3, the maximum absorption has occurred at wavelength (λ_{max}) 214.500 nm. The band gap of $Cd_xCu_{(1-x)}C_4H_4O_6$ crystal can be calculated as,

$$E_g \text{ in eV} = \frac{hc}{\lambda_{max}} = \frac{1240}{214.500} = 5.780 \text{ eV}$$

The energy band gap of grown $Cd_xCu_{(1-x)}C_4H_4O_6$ is 5.780eV. The high absorption in the ultra-violet region at about 214.500 nm makes the material is good for UV absorbers or filters and the wide transmission in the entire visible region enables it suitable candidate for optoelectronic applications.

3.2.2. 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 4. Single intense peak at 503.2438 nm is seen in PL spectrum of $Cd_xCu_{(1-x)}C_4H_4O_6$ as shown in figure 4.

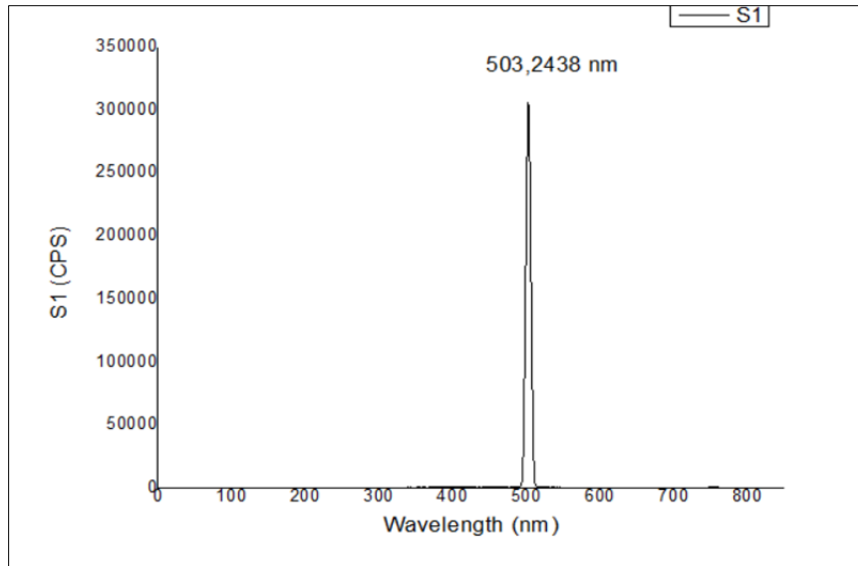


Figure 4 PL Spectrum of $Cd_xCu_{(1-x)}C_4H_4O_6$

This peak is 503.2438 nm which is close to value 508.6 nm reported [2]. An emission peak at 554 nm is found in the PL spectrum conforming to the copper oxide film, while it was shifted at 502 nm for the metal oxide composite sample [14].

It is transparent only for 503.2438, this may make it a filter at this UV-Visible wavelength or window application.

This peak is 503.2438 nm s close to sharp, intense transmission maxima peak at wavelength nearly 505.03876 nm of pure Copper tartrate which is close to value 508.6 nm reported [2]. Hence, transmission is from UV to Visible range mostly Blue in color. It is showing transparency of copper tartrate crystals to Visible range of electromagnetic radiation. This emission originates from Cu^{2+} vacancy-related defects or their complexes. The green Cu emission has been extensively studied by Shinoya and co-workers [15].

3.3. 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.

3.3.1. Thermogravimetric Analysis (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 observed weight loss of sample is compared with theoretical values to analyze decomposition reaction as below:

The sample loose or gain weight on heating due to different processes on heating. The mechanisms of weight change are:

- Weight Loss:
 - Decomposition
 - Evaporation
 - Reduction
 - Desorption
- Weight Gain:
 - Oxidation
 - Absorption or Adsorption

- 3) Thermogram of Cd doped Copper Tartrate ($Cd_xCu_{(1-x)}C_4H_4O_6$) 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 5.

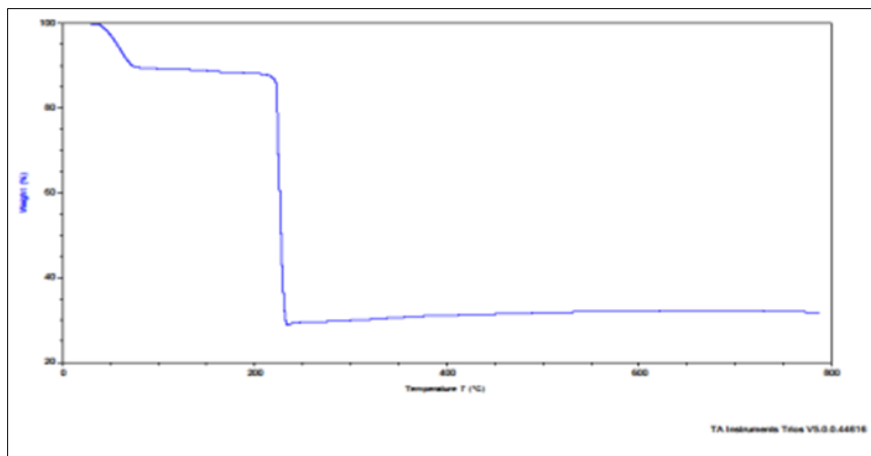


Figure 5 TGA Curve of Cadmium doped Copper tartrate

The possible interpretation of parts of a thermogram can be classified as curve in Figure 5 as illustrated in the table 4 below assigning them corresponding reaction over a corresponding temperature range [16].

TGA analysis curve in figure 5 indicate loss of mass as below as illustrated in table 4.

At the room temperature mass is 100%. Between temperature range $89.01^{\circ}C - 224.03^{\circ}C$ it is 72.015% close to theoretical mass of $Cd_{0.03}Cu_{0.97}C_4H_4O_6$. One can say that there is loss of this molecule at small steps via $2CO_2 + CH_4 + CO$.

At the temperature $228.97^{\circ}C$, there is loss of $\frac{1}{2}H_2O$ and remaining sample has observed mass of Cd doped CuO as 32.859%.

One may conclude that, sample is stable up to $224.03^{\circ}C$.

Table 4 Decomposition Analysis of Cd doped Copper tartrate From TGA Curve at Ramp $20^{\circ}C/min$ to $800^{\circ}C$

Sample	Temperature (°C)	Decomposition of single crystals	Theoretical Weight of present sample (%)	Observed Weight (%)
Cadmium doped Copper Tartrate	Room Temperature	$Cd_{0.03}Cu_{0.97}C_4H_4O_6 \cdot \frac{1}{2}H_2O$	100%	100%
	$89.01^{\circ}C - 224.03^{\circ}C$	$Cd_{0.03}Cu_{0.97} \cdot \frac{1}{2}H_2O$	72.477%	72.015%
	$228.97^{\circ}C$	$Cd_{0.03}Cu_{0.97}O$	29.27%	32.926%

The Single crystal material of Cadmium doped Copper tartrate is stable up to $224.03^{\circ}C$

3.3.2. 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, from 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, aluminium pan is used to put the weighed sample powder. The surrounding medium was air. The sample was heated at the rate of 20⁰ Cel/min up to 350⁰Cel. 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 of simple or complex materials which can be compared for identification of materials using measurements of peak positions, sizes or shapes.

DSC analysis of the grown crystals was recorded between 0.210371047 Cel to 350 Cel in the nitrogen atmosphere and the heating rate was maintained at 20 Cel /min.

In the DSC curve, we can observe three endothermic peaks at 96.7 Cel, 277.4 cel, 314.5 Cel and one exothermic peak at 286.2 Cel. The DSC data collected from the DSC curve is shown in Fig.6 and illustrated in the table.5 below:

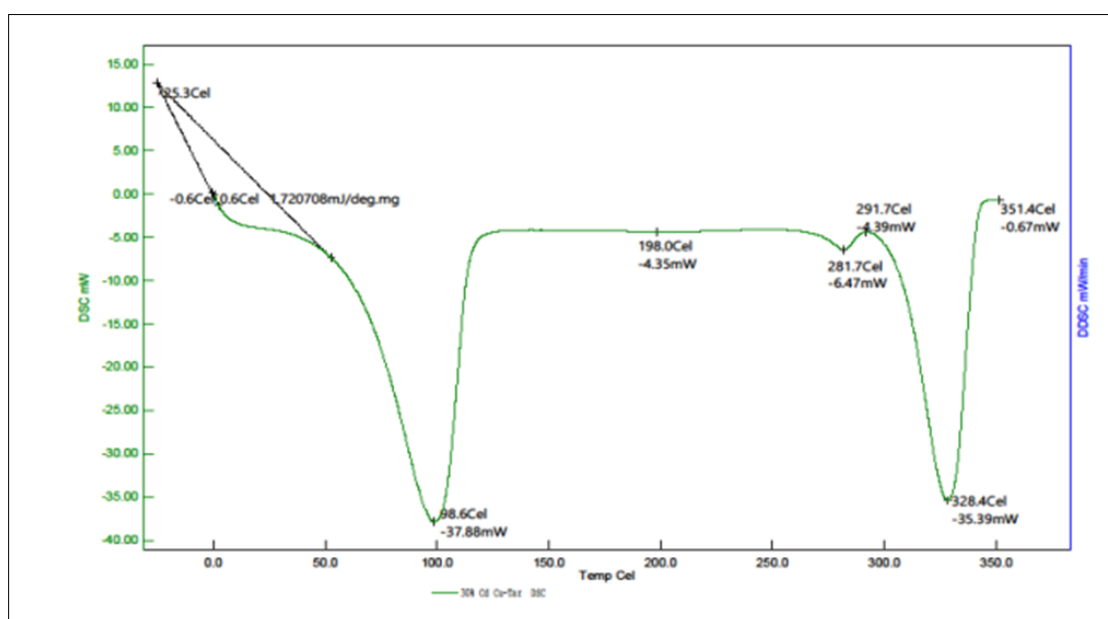


Figure 6 DSC Analysis Curve of $Cd_xCu_{1-x}C_4H_4O_6 \cdot nH_2O$

Endothermic and exothermic peaks observed in DSC curve are analyzed as represented in the table 5.

Table 5 Data from DSC Curve analysis [17] of $Cd_xCu_{1-x}C_4H_4O_6 \cdot nH_2O$

Sample	Peaks	Temperature (Cel)	Remark
$Cd_xCu_{1-x}C_4H_4O_6 \cdot nH_2O$	Endothermic	1)98.6 Cel (TGA%wt89.303 at 98.61Celcius)	1)Energy absorbed during a loss of H_2O
		2)281.7 Cel	2)Decomposition of $C_4H_4O_6^{2-}$ to $C_4H_4O_6$ and O_2
		3)328.4 Cel	3)decomposition of $C_4H_4O_6$ to CH_2 , H_2O , CO , C_2H_2 and CH_2O
	Exothermic	291.7(TGA%wt29.848 at 291.71celcius)	due to conversion of $C_4H_4O_6^{2-}$ into an isomeride with a hexatomic ring and Oxidation of Cu Species
		351.4(TGA%wt30.594)	Wt. of Cd doped CuO

From the thermogram, the temperature value 328.4 Cel may be assigned to apparent melting and apparent latent heat of fusion is determined as 35.39 mw. The endothermic peak at 98.6 Cel 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 98.6 Cel 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 vapour 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 98.6 Cel. The exothermic peak at 291.7 Cel is due to the decomposition of Cd doped 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 Cd doped CuO molecules in the TGA curve. In order to decomposition into the Carboxylate ion and Cd doped CuO some old bonds are break and new bonds are formed to make $C_4H_4O_6^{(2-)}$ 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 351.4 Cel [17].

4. Conclusion

Cadmium doped copper tartrate crystals can be grown by 'Gel Growth technique' by single diffusion in Silica gel of optimum specific gravity 1.04 g/ml set with tartaric acid at optimum pH of 4 and aging period for 4 days .Band gap of copper tartrate crystal is determined using Ultraviolet-Visible Spectroscopy is 5.780 eV. Blue Color of Copper tartrate crystal and transparency is confirmed using Photoluminescence spectroscopy. Emission originate from Cu^{2+} vacancy-related defects or their complexes. Dimensions of crystals are found from Powder X-Ray Diffraction data. The edge lengths of unit cell calculated from indexing of PXRD data are, $a = 5.47 \text{ \AA}$, $b = 11.76 \text{ \AA}$, $c = 9.20 \text{ \AA}$ and volume of unit cell is, 621.02208 \AA^3 . From the thermogram, the temperature value 328.4 Cel may be assigned to apparent melting and apparent latent heat of fusion is determined as 35.39 mw.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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