



OPTICAL THERMAL AND KINETICS OF COPPER IODIDE GROWN CRYSTAL IN GEL AND ITS CHARACTERISATION.

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Abstract: A crystal of copper iodide have been grown by single and alternate diffusion in gel, A multishaped bigger sized tetragonal crystal were obtained, for this alternative supernatants, incorporating solutions its concentrations effects on growth of these crystals studied. Structural analysis optimum condition, lattice parameters infra radiations, thermal characterizations were performed. In the present work, an attempt has been made to characterize gel grown crystals of copper iodide by X-ray diffractometry, infrared spectroscopy, Thermal analysis i.e. TGA and DSC.

Key words: X-ray diffraction, FT-IR, Thermal TGA, DSC, Gel technique, Unit cell.

1.1 Introduction:

Crystal growth is an interdisciplinary area, which is the key to the development of crystallography, solid state physics, and material science. Hence, enormous amount of research work has been lavished for growth of bigger, perfect, and pure crystals. Crystal of iodide exhibit nonlinear optical properties and found variety of applications in many areas of modern science, technology and engineering. In recent years, some researchers were tried study the growth and characterization of iodide crystals. Recently attention was drawn to different salts of iodic acid in view of their piezoelectric and electro-optical applications. Hence, the growth of crystals of copper iodide by gel technique by single diffusion method is reported in this chapter. The present chapter reviews several aspects regarding the growth procedure of copper iodide; optimum growth conditions and the kinetics i.e. influence of different growth parameters to obtain optimization condition for the growth of these crystals. This chapter also predicts the results obtained from the different techniques used for the characterization of gel grown crystals of copper iodide. Copper iodide crystals cannot crystallize by high temperature methods, as the material starts decomposing before melting. Therefore conventional high temperature methods for its growth required crystals are not applicable. Gel method is the only alternative technique to grow the crystals of the appreciable size and quality as reported in the present work at ambient temperature. Moreover, this method is simple and inexpensive. Hence the crystals of copper iodide were grown by gel method. 4.2. Crystal growth of copper iodide: The growth of copper iodide crystal in gel media is based on the diffusion method. In the present work, an attempt has been made to characterize gel grown crystals of copper iodide by X-ray diffractometry, infrared spectroscopy, Thermal analysis i.e. TGA and DSC.

1.2 Experimental procedure:

Copper iodide crystals are grown using chemical reaction method. In this experiment gel containing copper chloride with different concentrations and copper iodide used as a supernatant hence the crystal growth occurred. 4.2.

For the preparation of gel, Initially different molar solutions of sodium meta silicate solutions taken for e.g. 10gm, 11 gm., 12gm, 13gm, 1gm, 16gm, 18gm, 20gm in distilled water to get solution 250cc, The solution is constantly stirred and then filtered by Dr watts filter paper .It was then kept in to an air tight bottle free from dust and contamination. Density of the solution was measured using specific gravity bottle and solutions of required molarities of copper chloride, copper nitrate, and potassium iodide were prepared by adding proper amount of chemicals to the double distilled water. In the present work, the solutions of sodium Meta silicate is mixed with various concentrations of acetic acid were tried. A gel formation takes place due to the polymerization in the resultant solution. 4.2. A gel containing potassium iodide was prepared by using various concentrations of sodium Meta silicate and acetic acid .For this purpose, 5cc, of 2N acetic acid was taken in a beaker, to which sodium Meta silicate solution having different densities was added drop wise with the help of burette. During this procedure the solutions was continuously stirred by means of magnetic stirrer so as to avoid premature local gelling .Then 5cc potassium iodide solution of different molarities were added to this mixture with constant stirring to make the solution homogeneous. The pH of the mixture was maintained at 4.4 .The number of attempts were carried out to optimized suitable pH value for growth of good quality crystals. This mixture was then transferred to the test tube. The test tube was then covered by cotton plug to avoid contamination of the exposed surface with atmospheric impurities and to keep the gel at atmospheric conditions .The gel was allowed to set .It took nearly 15 days for setting .This set gel was allowed to age for 4days Aging helps to controlled the nucleation caused due to reduction in diameter of the capillaries in gel. Copper chloride was used as supernatant. The different molarities of supernatant were prepared and added over the set gel of potassium iodide. Experiments were also carried out by exchanging the positions of reactants and supernatants.

The chemical reaction inside the gel as follows: $XCl_2 + KI = XI + YCl_2$ Where X=Cu and Y=K

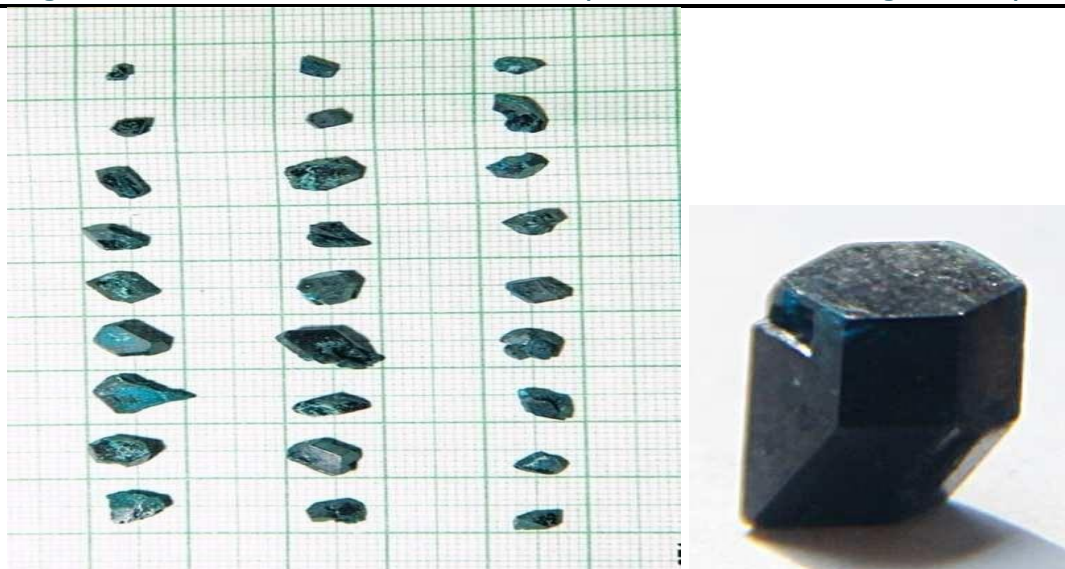


Figure 1.0 Number of grown crystals of copper iodide

1.3 Nucleation:-

A formation of nuclei depends on number of parameters such as pH of solution maintained, concentrations of reactants, aging of gel, density of gel. It was observed that initial nucleation of this gel takes place on the surface of the gel and rarely inside the gel. Nucleation of copper nitrate or copper chloride gel takes place after 9 to 12 days. Generally this time varies few hours too few days depending upon the ambient temperature

1.4 Result and Discussions:

Many trials are performed to obtain optimum condition for growing copper iodide crystals. A bigger size only one crystal was grown in gel medium shown in figure. But, in some cases numbers of crystals of different in sizes are grown inside the gel. It is due to the effect of pH and potassium iodide used as supernatant. Increase in aging of gel reduces number of nucleation centers. Insufficient gel aging often may leads to the fracturing of gel. Higher pH value of gel sets early but crystals obtained are less transparent due to the inclusion of silica gel. When pH less than 4.2, gel takes longer time to set and there is possibility of breaking of gel. Higher concentrations of reactants results on size and quality of crystals near the gel interface. Less concentrations of reactants leads to diminished the formations of size in crystals. Hence, Increase in aging of gel reduces number of nucleation centers and growth rate. Insufficient gel aging often leads to the fracturing of gel at the time of addition of supernatant. 4.4.



Figure 1.1 spherulite crystals are grown in gel

The size of grown crystals of 0.5cm X0.8cm X1.2cm. Some time at higher pH equal to 4.5, bigger crystal of size 2cm were obtained. Copper iodide crystals of different size and shape shown in figure 1.0, which are multi shaped crystal. The whitish and spherical crystals are grown in gel containing copper nitrate shown in figure 1.1

1.5. Observations:

In present work potassium iodide, copper chloride and copper nitrate are used as a reactant as shown in figure 1.1 spherical shaped shining number of white crystals are observed, in this case when potassium iodide was used as supernatant. The crowded micro crystals are obtained because of higher concentrations of supernatants. By reducing the concentration of supernatant, quality of the grown crystals can be improved. The crystals grown are at the interface and in the gel, but small size crystals of CuI they are attached to the wall of test tube in some cases. A gel containing copper chloride instead of copper nitrate, it is observed that, the colour in gel turns from red to faint black and transparency of grown crystals was increased. In the test tube of increasing pH the only one bigger size crystal is seen. In this case copper chloride used as supernatant. It is observed that alternation or exchange of same solutions shows surprising effect on growing in size and quality of copper iodide crystals. The size of grown crystals of 0.5cm X0.8cm X1.2cm. Some time at higher pH equal to 4.5, bigger crystal of size 2cm were obtained. Copper iodide crystals of different size and shape shown in figure 1.3. which are multi shaped crystal. The whitish and spherical crystals are grown in gel containing copper nitrate.



Figure 1.3 bigger size crystals of copper iodide

2.1. X-ray diffraction (XRD) :

X-ray diffractogram is useful in the analysis of crystal structure, d-values, cell parameters, unit cell volume and lattice system etc. can be evaluated using X-ray diffractogram. When the high frequency electromagnetic waves are selected to have wavelength comparable to the interplaner spacing of the crystals, they are diffracted according to the physical laws. The interplaner spacing (d) can be calculated to four digits and even more significant figures by measuring the diffraction angles. This, in turn, can be used to determine cell parameters and the system to which the sample under study belongs, etc. the reflecting planes in crystal h, k, l values can be calculated (5).

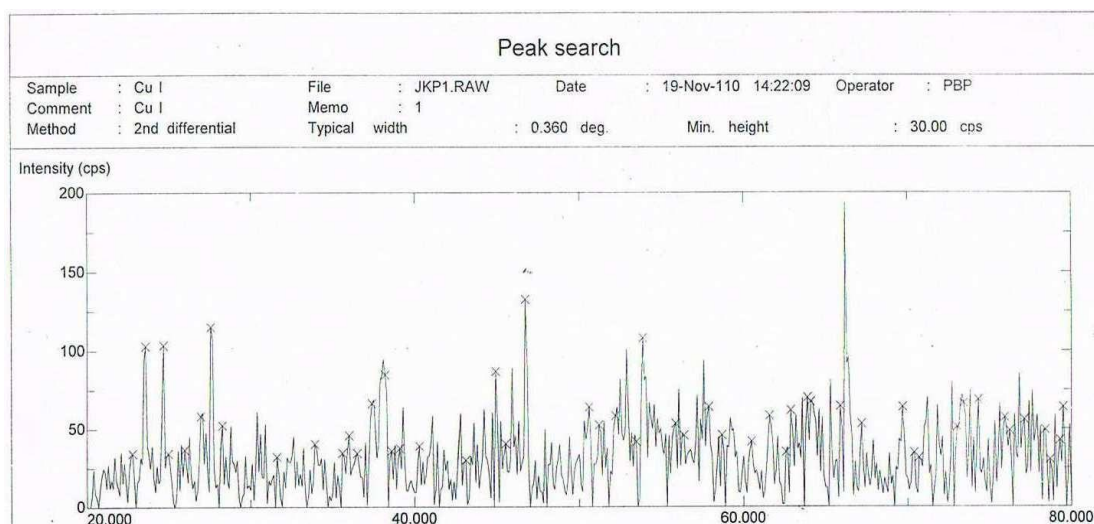


Figure 1.4 X-ray Diffract gram of copper iodide

X-ray diffractogram of gel grown crystal of copper iodide was recorded using Minislex model, Japan with Cuka radiation of wave length 1.5408 \AA and scanning speed of $10^\circ/\text{minute}$. A copper target and nickel filter were used From the powder diffractogram on data of copper iodide which shows twenty different peaks and corresponding d values and (h k l) values were computed by using computer program POWD [An interactive powder diffraction data interpretation and indexing program] The recorded X-ray diffractogram is as shown in fig. 1.4The study was carried out at Department of Physical sciences, North Maharashtra University Jalgaon, Maharashtra. These values are computed using computer programmed, POWD is as shown in the table 1.1. From POWD it found the lattice parameter of unit cell satisfy condition $a \neq b \neq c$ and $\alpha = \beta = 90$ and $\gamma \neq 90$. so unit cell structure is Tetragonal Calculated unit cell lattice parameter of the copper iodide crystal are given in table 1.1 as follows

Table 1.1 : Lattice Parameters:

Copper iodide	Parameters
System	Tetragonal
a	10.6536 \AA
b	10.6496 \AA
c	12.5612 \AA
α	90°
β	1.1791 \AA
γ	90°
V	$1425.67 (\text{ \AA}^3)$

2.2 FT-IR of Copper Iodide :

IR spectra of gel grown copper iodide crystal was recorded in the wave number range 500 to 4000 cm^{-1} for KBr line. The spectrum of copper iodide is as shown in figure 1.6 , the bands 3416.05 cm^{-1} are due to OH-stretching band of N-H group, the band 3271.38 cm^{-1} is hydrogen bonded of C-H stretching. The region of these bands from 3416.05 cm^{-1} shows characteristic frequency. The band 1608.69 cm^{-1} shows N-H band of ant symmetric deformation in NH_3 .A peak of 1444.73 cm^{-1} shows existence of $\text{CH}_3\text{-C}$ group of nitro compounds with co-o stretching. A Strong stretching vibration is occur in 1039.67 cm^{-1} due to -C-OH stretching frequency of C-O bond. A band of 692.47 cm^{-1} is rocking vibration stretching which shows metal oxygen bond. A region of bands 1444.73 cm^{-1} to 692.47 cm^{-1} shows fingerprint region. It is the existence of metal oxygen bond. The Vibrational different frequencies for the gel grown copper Iodide crystal are represented in copper iodide spectral

assignment:

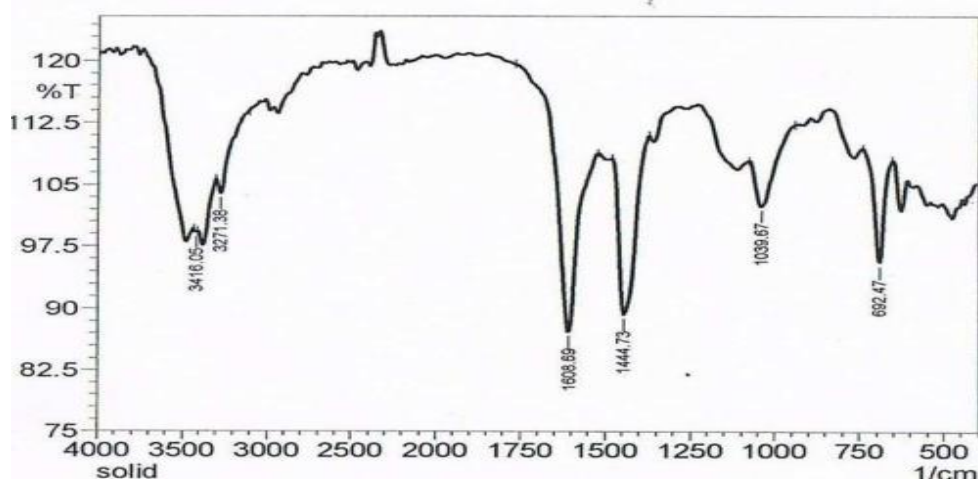


Figure 1.6 FT-IR spectrum of copper iodide.

2.2 Spectral assignment of the peak of copper iodide:

Sr. No.	Wave number (cm ⁻¹)	Assignment
1	3416.05 cm ⁻¹	OH- Stretching of NH group
2	3271.38 cm ⁻¹	C-H Stretching
3	1608.69 cm ⁻¹	N-H band
4	1444.73 cm ⁻¹	CH-3 group coo ⁻ stretching
5	1039.67 cm ⁻¹	C-OH stretching

2.3 Thermal analysis of copper iodide:

In the present work Thermal analysis of copper iodide crystal is done by methods using two techniques a) Thermogravimetry Analysis (TGA) and b) Differential scanning calorimetry (DSC). Which are widely used in the investigation of both chemical and physical phenomena The Thermogravimetry Analysis study is based on the observation of weight as a function of temperature. DSC Study depends on the measurement of difference in heat content of a sample with reference to a standard substance as a function of temperature.

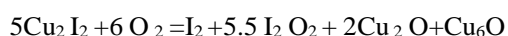
The TGA and DSC and FTIR study has been carried out and Recrystallized alumina sample holders were used and the heating rate of 10⁰ c/min. The TGA thermo gram was recorded in the temperature range from 20⁰c to 600⁰c microcrystalline (powdered) sample of copper iodide crystals was taken for TGA studies. The sample was hold for 1 min to 20⁰ c to evaporate water due to moisture and then heated from 20⁰ c to 600⁰ c at the rate of 10⁰ c/min.

The DSC thermo gram was recorded in the temperature range from 20⁰c to 300⁰c. Microcrystalline powdered samples of copper iodate crystals was held for 1min at 20⁰ c to evaporated water due to moisture and then heated from 20⁰c to 300⁰c at the rate of 10⁰c / min .After reaching the temperature of 300⁰ c the sample was hold for 1 minute at 300⁰ c and then again cooled from 300⁰ c to 20⁰ c the rate of 10⁰c/ min

2.4 Thermo Gravimetric Analysis (TGA):

It was confirmed that the thermal decomposition of copper iodide passes through an intermediate 5Cu₂ I₂, which is unstable and finally decomposes to Cu₆O. Curve for copper iodide gel grown crystals is as shown in the figure 1.7 by continuous line. The TGA data collected from this curve and the theoretical values as calculated from molecular formula using the reaction are listed in a table 4.9.

Reaction:



TGA curve of copper iodide showed clearly three stages of decomposition. TGA curve did not show an appreciable weight change in the temperature range 22⁰c to 99⁰c. Indicating that the crystals of copper iodide are thermally stable in this range. The calculated weight loss shown in the observation table 2.3. Calculated weight loss from the chemical formula has been estimated by following reaction at different temperatures.

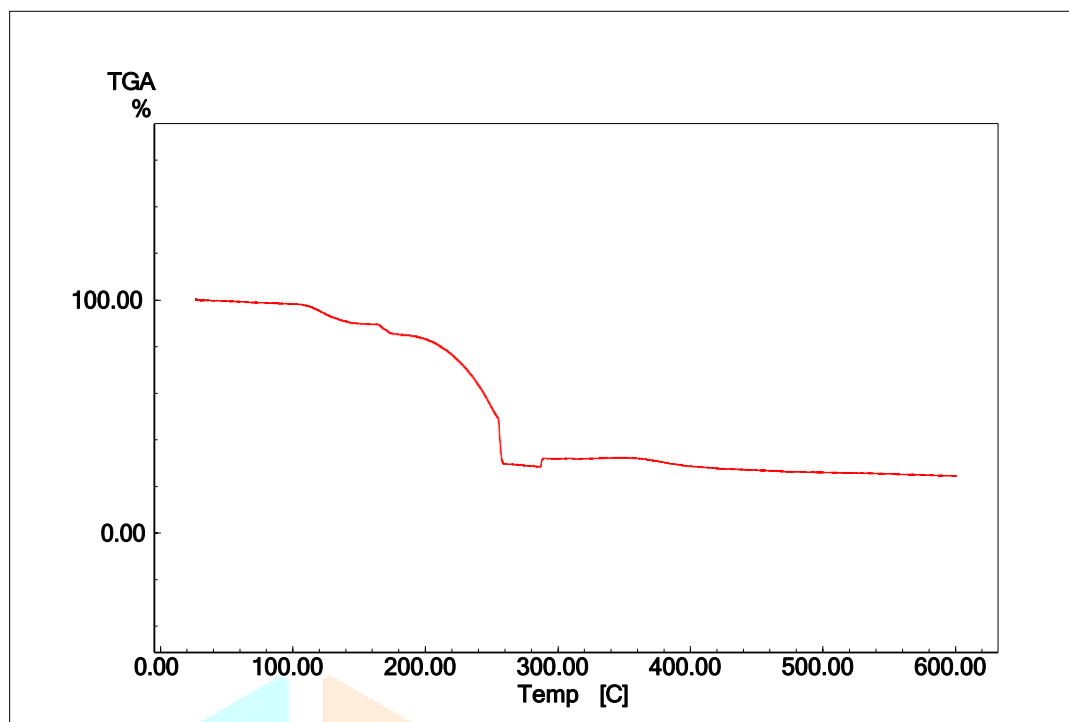


Figure 1.7 TGA of copper iodide

Table 2.3: TGA data of copper iodide crystals

Stage	Temperature range (0 C)	Observed weight loss %	Calculated weight loss %	Probable loss of water molecules
1	99.5 ⁰ c to 160.70 ⁰ c	12.07%	12.10%	1 I ₂
2	220.0 ⁰ c to 280 ⁰ c	73.912 %	74.99%	5.5 I ₂ and O ₂
3	Residue	14.01 %	13 %	2Cu ₂ O

2.5 Differential Scanning Calorimetry (DSC):

In DSC, the range of temperature for experimentation is 80⁰c to 1000⁰C. These methods are widely used in chemical analysis and for obtaining thermodynamic and kinetic data. Number of reviews is available on application of thermodynamic methods.

The DSC curve for copper iodide gel grown crystals is as shown in the figure 1.8. In DSC curve we can observe two endothermic peaks at 147.76⁰ C and 262.16⁰ C. However an exothermic peak was not noticed. The endothermic peak at 147.76⁰C is due to the decomposition of copper iodide losing one I₂ iodine molecule. In the first stage of decomposition, peak at 147.76⁰ C is attributed to the loss of one I₂ molecule. This endothermic peak observed in the DSC curve corresponding to the weight loss of one I₂ molecules in the TG curve. The endothermic peak at 262.16⁰ C is due to the decomposition of compound and this peak in the second stage of decomposition is attributed to the loss of one O₂ and 5.5 I₂. This endothermic peak observed in the DSC curve corresponding to the weight loss of one oxygen and 5.5 iodine molecules in the TGA curve. The endothermic peaks above 280.90⁰ C and 600⁰ C are due to the decomposition of compound and these peaks shows decomposition may be attributed to the loss of remaining part of the iodine. These endothermic peaks observed in the DSC curve correspond to the weight loss of iodine molecules in the TGA curve. Beyond the temperature 600⁰ C, the reaction proceeds and finally stable residue 2Cu₂O remains up to the end of analysis.

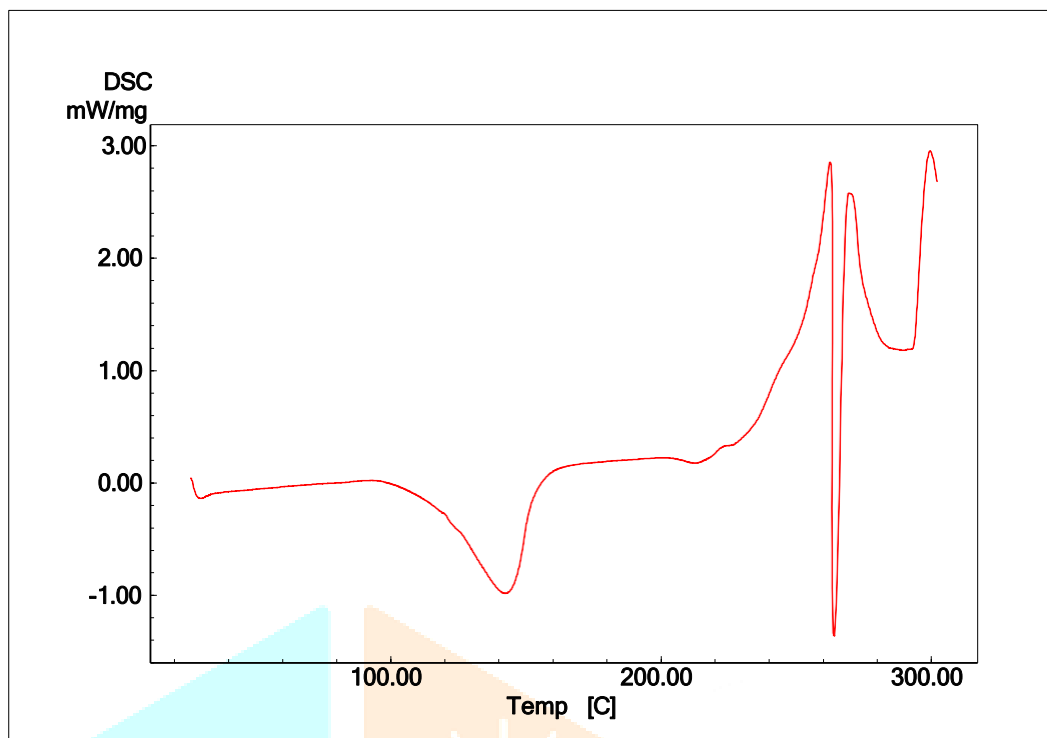


Figure 1.8: DSC of Copper Iodide

2.6 Conclusions:

1. The crystal of copper iodide can be grown by using gel technique Single diffusion gel Growth technique is suitable copper iodide crystals.
2. Different habits of copper iodide crystals can be obtained by changing their parameters.
3. Chemical composition of the grown crystal by chemical analysis and EDAX match with the theoretical calculation from molecular formula.
4. Unit cell parameter value and d values match very well with the reported ones
5. The structure of copper iodide is tetragonal confirmed by x-ray diffraction.
6. FT-IR analysis confirms the presence of fundamental infra-red frequencies, generally Observed in all iodide compounds.
7. TGA and DSC analysis confirms the presence of copper in the grown crystals.
8. Water of crystallization is not present in grown crystal confirmed by TGA, DSC and FTIR analysis.
9. The optical band gap of copper iodide signs towards semiconducting material.

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