International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2022): 7.942

Thermal Characterisations of Grown Copper Iodate Crystal in Gel and Study of Its Parameters

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Abstract: ***A crystal of copper iodate have been grown by simple gel technique A cubical star shaped bigger sized crystal were obtained for this alternative supernatants, incorporating solutions are used. Its concentrations parameters affects on growth of these crystals. Structural analysis optimum condition, geldensity, thermal characterizations and its stages of copper iodate crystals are discussed.***

Keywords: X-ray diffraction, gel technique, unit cell TGA, DSC

1. Introduction

Growth of copper iodate crystals by gel method is an important technique for growing crystals of many substances. Most of the solid state investigators are use this method for growing well developed crystals. Gel technique is an effective and efficient process, which produces perfect and quality crystals for their use at minimum valuation [1].

In the present investigation, it is observed that Copper iodate crystals cannot be crystallized by high temperature methods, because the material starts decomposing before melting. Therefore conventional high temperature methods for its growth are not applicable. Gel method is only the alternative technique to grow the crystal of appreciable size and good quality as reported in the present work at ambient temperature. The present paper reviews several aspects regarding the growth procedure of copper iodate $Cu(IO_3)_2$ H_2O crystal, optimum growth conditions and the kinetics i.e. influence of different growth parameters to obtain optimization conditions for the growth of these crystals. This paper also predicts the results obtained from the different techniques used for the characterization of gel grown crystals of copper iodate [2].

2. Experimental Procedure

Initially, different concentration of solutions of sodium Meta silicate taken for e.g. 12gm, 20gm, and 21.5gm 23gm in distilled water to get 250cc solution. The solution is constantly stirred and then filtered by Dr Watts's filter paper. It is then kept in to an airtight bottle free from dust and contamination. Density of the solution was measured using specific gravity bottle. A solution of different molarities prepared by adding proper amount of chemicals to the double distilled water .The chemicals used are copper nitrate, copper chloride, potassium iodate, acetic acid and sodium meta silicate. When the solution of sodium Meta silicate is mixed with any of mineral or organic acid, gel formation takes place due to the polymerization in the resultant solution. In the present work, various concentrations of acetic acid, copper chloride, potassium iodate used with sodium Meta silicate tried for optimum condition to obtain good quality crystals of copper iodate.

3. Single Diffusion Method

This method used to obtain good quality crystal of copper iodate in gel medium. In actual procedure, 5cc of 2N acetic acid was taken in a small beaker, to which sodium meta silicate solution of density 1.04 gm/cc was added drop by drop with constant stirring by using magnetic stirrer, till pH of the solution reaches a value 4.4. A digital pocket sized pH meter of HANNA instrument is used for this purpose. A 5cc of copper nitrate solution was added with constant stirring in mixture of acetic acid and sodium Meta silicate solution. The pH of the mixture was maintained at 4.3, Number of experiments were carried out to secure appropriate range of pH values which in turn gives good gel allowing to grow good quality crystals [3].

It was observed that the mixture of solution with pH value less than 4.2, gelation takes quiet large time of the order of several days. However in the pH range 4.2 to 4.5, there was appropriate waiting in gelation time. The gel setting time required for the gel solutions of pH greater than 4.5 was short. Borosil glass test tubes of diameter 2.5cm and height 25cm were used as crystallizing vessels. This mixture was then transferred to the test tube, a mouth of test tube closed using cotton plug used to avoid contamination of the exposed surface with atmospheric impurities and to keep the gel at atmospheric conditions.

Initially the mixture appeared in test tube was bluish, However with lapse of time its color changed towards dark blue when gel was completely set. The setting time was 10-12days. The completely set gel was left for aging for 96 hours to120 hours. It is also observed that the aging of gel reduces the diameter of the capillaries in gel so that speed of the reaction is automatically controlled. Potassium iodate was used as supernatant having different molarities like 0.1M, 0.4M, 0.5M. 1M. were added over the copper chloride set gel.

As the concentrations of supernatant increases, the numbers of nucleation centers were also found to be increased. For this, numbers of test tubes were set up for the observation. Alternation method of supernatant and reactant also used to obtain good quality crystal of copper iodate [4].

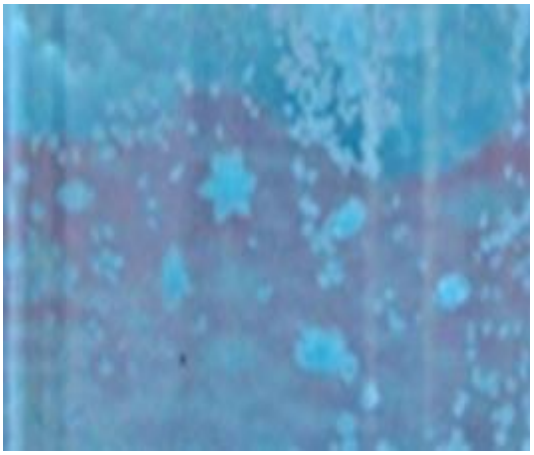

Figure 1.1: Star shaped crystal of copper chloride

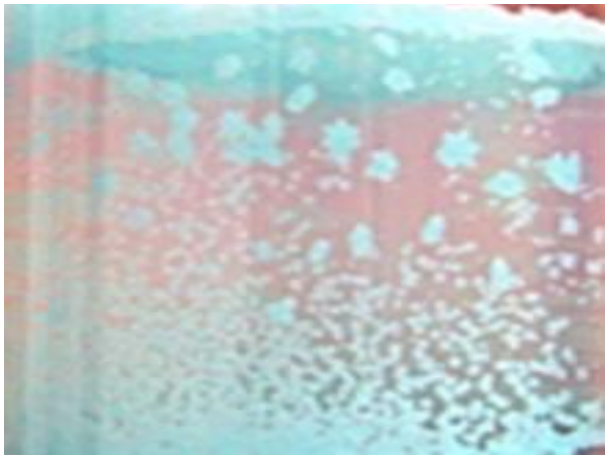

Figure 1.2: Star shaped crystal of copper nitrate

4. Result and discussion

The optimum growth conditions for the growth of copper iodate crystals are represented in Table1.1. Different parameters such as gel density, gel setting time, gel aging time, concentration of reactant, pH of gel, period of growth have the considerable effect on the growth rate.

Copper nitrate and copper chloride solutions are used to compared thickness transparency and quality of the crystal. The thickness of crystals grown by using copper nitrate as reactant is quiet effective in comparison when copper chloride is used as reactant. A shape of copper iodate crystals in gel containing copper nitrate turns from spherical to star shaped are crowded The size of copper iodate crystal in nitrate gel is small but are also transparent.

Table 1.1: Optimum Parameters

Condition Lattice parameter	Copper iodate concentrations
Density of sodium Meta silicate	1.04kg/m^3
pH of mixture	4.2
Amount of 2N acetic acid	5ml
Temperature	Room temperature
Gel setting time	10 days
Gel aging time	4 days
Concentration of KIO_3	0.4M
Concentration of $CuCl_2$	1M
Concentration of $Cu(NO_3)_2$	1M
Period of growth	3 weeks

5. Observations

Figures shows different forms of grown copper iodate crystals for the different concentrations of $CuCl_2$ solution in the gel. The range of the $CuCl_2$ Solution used was from 0.1 M to 0.5 M .The whisker growth with greater length originating from the interface of the gel was observed in the test tube containing $CuCl_2$ solution of 0.1M. However the dendritic crystal growth was not observed in the test tube containing $CuCl_2$ solution of 0.1 M concentration. As the concentration of $CuCl_2$ solution was increased up to 0.4M, it leads to dendritic growth along with the whisker growth .However there was no growth of shaped crystals. It was observed that in a test tube containing $CuCl_2$ solution of 0.5 M concentration, growth of copper iodate occurs in three phases which are whisker, cubical and star shaped. In present work, potassium iodate used as supernatant, starshaped one beautiful (2mm) shinning crystal is observed. In the Figure few circular Shaped Crowded Crystals are seen. Large numbers of circular shaped small tiny crystals are seen at the wall of test tube. But at interface large, very crowded crystals are seen. The layer of crystals is very thick. The region of interface and region of crystal has turned transparent instead of blue i.e. the region in which copper nitrate has been completely utilized for crystallization.

Effect of pH on gel

This is one of the effective parameter of crystal growth. A value of pH directly affects on transparency of growing crystal and gelation of solution contain in test tube. By changing the pH of gel without changing gel composition and concentration of reactants, the effect of pH on growth rate was studied. The pH value of gel was varied from 2.5 to 7.0.A crystal growing at higher values of pH were not transparent and well defined. This may be due to contamination of the crystals with silica gel. This is because as pH increases, the gel structure changes from distinctly boxlike network to a structure of loosely bound platelets, which appear to lack cross linkages and the cellular nature becomes less distinct. Number of nuclei also decreases and the crystals of copper iodate are not well defined, due to improper formation of cells at high pH values [5].

Gel takes longer time to set with smaller pH values .Such gel can be easily fractured at the time of addition of supernatant. The effect of the different pH values on gel setting time observed .and the quality of grown crystal is as shown in Table 1.1. The optimum value of gel pH to get ideal gel is found to be 4.3 .At pH values less than 4.4 the time for gelation increased, and the resultant gel was unstable, for pH values greater than 4.4, the gelation occurred very soon and the resultant gel was not transparent. Figure 1.3 shows the graph of nucleation densityagainst the gel aging time [6].

In the present work, pH value of 4.3 is the optimum condition for the good quality crystal of copper iodate.

Effect of gel aging

Gel aging is one of the effective parameter in crystal growth. To study the effect of aging on gels, gel of same pH and density were allowed to age for various periods. A feed solution of constant molarity was then added over a set gel. It is found that the number of copper iodate crystals

decreases as the aging of gel increases. Aging of gel decreases the diffusion and nucleation density. More aging causes more amount of water evaporation out of the gel. The effect of water evaporation should be considered before and after the formation of gel. Before the gel is set, the evaporation of water causes an increase in gel density which in turn decreases the diffusivity of reactive ions in the gel [7].

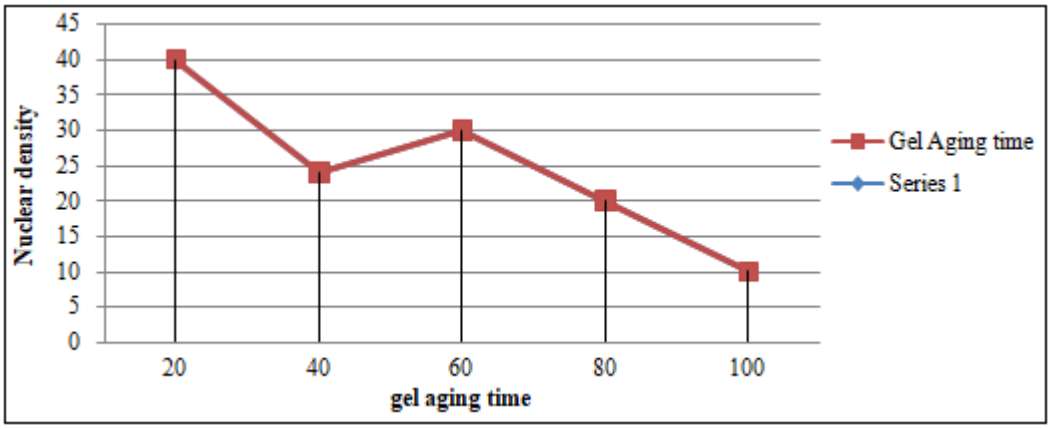

Figure 1.3: Nucleation density with gel aging time

X-ray diffract meter (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. 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 inter planer spacing (d) can be calculated to four digits and even more significant figures by

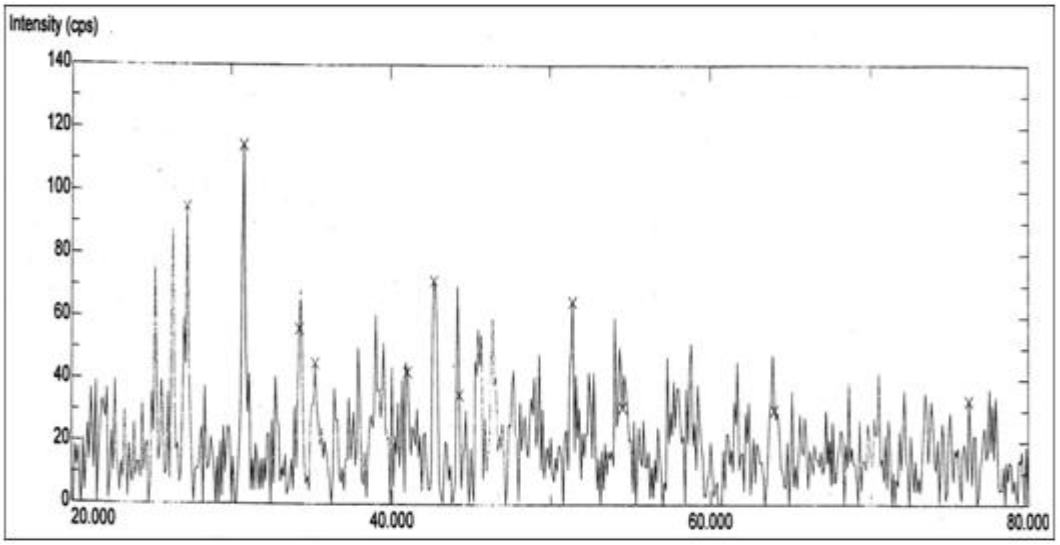

Figure 1.4: X-ray powder Diffraction data of copper iodate crystal

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. [8]

X-ray diffractogram of gel grown crystal of copper iodate was recorded using Miniflex model, Japan with Cukα radiation of wave length 1.5408°.A and scanning speed of 10 ^{0}/minute. A copper target and nickel filter were used. From the powder diffractogram on data of copper iodate which shows eleven different peaks as shown in figure 1.4, 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. 1.3 The study was carried out at Department of Physical sciences, North Maharashtra University Jalgaon, Maharashtra.

Table 1.2: X-ray Diffraction on copper iodate crystal

Peak No.	2Theta	FWHM	d-value	Intensity	I/I_0
1	27.200	0.706	3.2757	95	83
2	30.88	0.706	2.9005	115	100
3	34.200	0.706	2.6196	56	50
4	35.200	0.706	2.5474	45	40
5	41.000	0.941	2.1994	42	38
6	42.700	0.706	2.1157	71	63
7	44.300	0.706	2.0429	35	31
8	51.400	0.706	1.7762	65	57
9	54.500	1.059	1.6822	31	28
10	64.000	0.706	1.4535	30	27
11	76.200	0.824	1.2483	33	29

These values are computed using computer programmed, POWD is as shown in the table These parameters satisfy the condition for monoclinic system. These calculated values agree with the reported ones .The observed peaks in deflection show that the copper iodate crystal possesses monoclinic structure (a≠b≠c and$\alpha=\gamma=90^{0.}$ and $\beta\#90^{0}$). Calculated unit cell lattice parameter of the copper iodate crystal are given in table 1.2

Thermo Gravimetric Analysis (TGA):-

The TGA thermo gram was recorded in the temperature range from 20^{0}c to 600^{0} c microcrystalline (powdered) sample of copper iodate crystals were taken for TGA studies. The sample was hold for 1 min at 20 ^{0}c to evaporate water due to moisture and then heated from 20^{0} c to 600^{0} c at the rate of 10^{0} c/min.

The DSC thermo gram was recorded in the temperature range from 20^{0}c to 300°c. Microcrystalline powdered samples of copper iodate crystal s were held for 1min at 20^{0} c to evaporated water due to moisture and then heated from20^{0}c to300^{0}c at the rate of 10^{0}c / min .After reaching the temperature of 300^{0} c the sample was hold for 1 minute at 300^{0} c and then again cooled from 300^{0} c to 20^{0} c the rate of 10 ^{0}c/ min. [9]

It was confirmed that the thermal decomposition of copper iodate passes through Cu_5 $(IO_6)_2$ which is unstable and immediately decomposes to Cu_5O It has a one stage course until CuO is obtained an intermediate orthoperiodate $Cu_5(Io_6)_2$ is obtained in this process analogously alkaline earth iodates, however unlike $Cu_5(Io_6)_2$, immediately after it is obtained begins to decompose to CuO.

Hydrous copper iodate becomes anhydrous according to reaction

$Cu(IO_3)_2 H_2O = Cu(IO_3)_2$.

Anhydrous copper iodate decompose at high temperature according to reaction

$5Cu(IO_3)_2 = Cu_5(IO_6)_2 \rightarrow 10_2 \uparrow + 0.5I_2 \uparrow + 110_2 \uparrow + 4.5I_2 \uparrow + 5CuO$

The TGA curve for copper iodate gel grown crystal is as shown in the figure 3.16 by continuous line. The TGA data collected from this curve and the theoretical values as calculated from molecules formula using the reaction are listed in a table

TGA curve of copper iodate showed clearly two stage of decomposition up to 600°c.TGA curve did not show an appreciable weight change in the temperature range 28°c to 98°c indicating that the crystals of copper iodate are thermally stable in this range .The first stage of decomposition occurs in the temperature range 98.5°c to 260°cin which weight loss of 6.018% agrees very well with the calculated weight loss of 6.36 %.

This clearly indicates that the crystal of copper iodate is hydrated and weight loss calculation clearly indicates its decomposition.

The probable loss of molecules in this stage are one O_2 and 0.5 I_2. Therefore the grown crystal becomes anhydrous at 210 ^{0}c.[10]

There is no further weight loss up to 340^{0} showing thermal stability of copper iodate crystals in the temperature range of 210 ^{0}c to 340^{0}c. The second stage of decomposition occurs in the temperature range 341.35^{0}c to 590^{0}c in which observed weight loss of 58.692 %, due to loss of 10_2 and 4.5 I_2 is observed. [11]This is in agreement with the calculated weight loss of 58.0680 %, which is confirmed by the observed residual weight. The observed residual weight of 35.290% up to the end of analysis. This is nearly agreement with the calculated residue weight of 34.0960%, This confirms the presence of copper in the grown crystals.

The calculated weight loss shown in the observation calculated weight loss from the chemical formula has been estimated by following reaction at different temperatures.

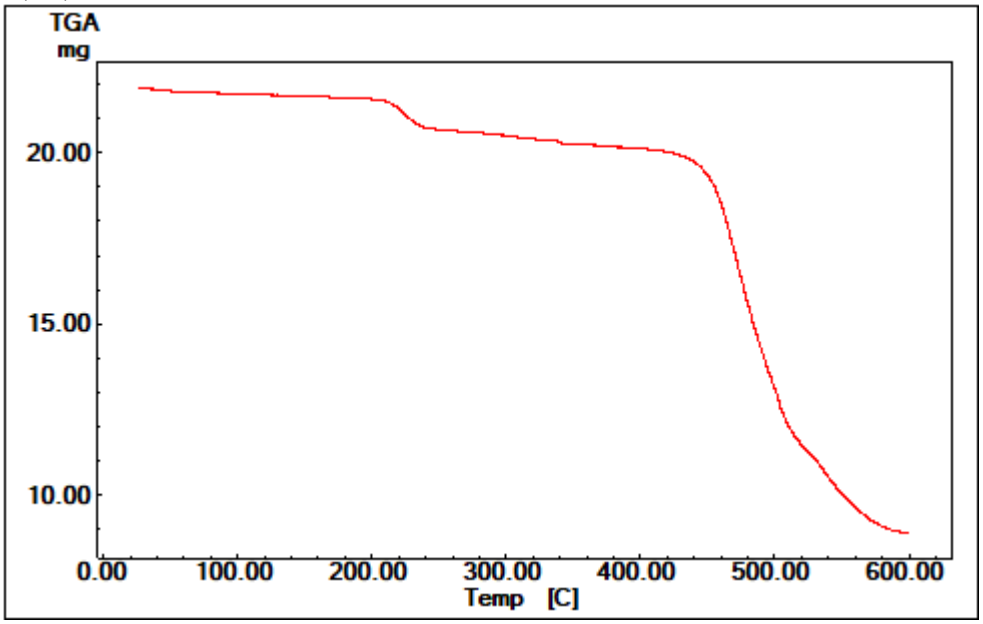

Figure 1.5: TGA of Copper Iodate

Tables 1.3: TGA data of copper iodate crystal.

Stage	Temperature range	Observed weight loss%	Calculatedweight loss%	Probable loss of molecules
1	98.5 ^{0}C to 260 ^{0}C	6.018%	6.36%	$10_2 + 0.5I_2$
2	340 ^{0}C to 590 ^{0}C	58.692%	58.013%	$11O_2 + 4.5\ I_2$
Stable residue weight (C_u O)		35.290	35.627	_

6. Conclusion

1) It is observed that the color of copper nitrate is dark blue as compare to copper chloride, copper chloride crystals are shining and transparent but both are star shaped.
2) Single diffusion gel growth technique is suitable to grow copper iodate crystals.
3) TGA and DSC analysis confirms the presence of copper in the grown crystals.
4) Water of crystallization is absent in grown crystal confirmed by TGA, DSC and FT-IR analysis
5) Star shaped copper iodate crystal can be grown by simple gel technique.
6) The effect of pH, concentration of reactants, gel aging and setting, gel density and room temperature is important to grown crystals.

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