Growth of Spherulite Starshaped Copper iodate Crystals in Gel and its effective kinetic Parameters

Kailas. P. Joshi.
Department of Physics, Dr.S.D.D. Arts College and Commerce and Science College Wada, Palghar

Abstract **- Copper iodate crystals of spherulite and Starshaped are grown using simple gel technique at ambient temperature. The various lattice parameters of grown crystals are obtained, gel aging time, gel setting time, Effect of pH observed, Different Parameters like, Gel density, Setting time, Gel Aging, Concentration programming, concentration of reactant, chemical Analysis, h,k,l values are determined,. Effect of Doping, Molar concentrations, PH of reactants and Alternate Diffusion methods in gel for size of crystal studied**

Index Terms **- Copper Crystal, spherulite, starshaped, Gel method; Doping, pH, setting time, Nucleation.**

I.INTRODUCTION

Growth of copper iodate crystals by gel method is a promising technique for growing crystals of many substances. Now a day, most of the solid-state investigations are made by using well developed crystals. An effective efficient process is one, which produces adequately perfect crystals for their use at minimum cost. In the present investigation, no reaction waste material is formed with in the gel. The aim of the present work is to put the gel method with standard performance and potentiality so that more perfect larger crystals should obtain at ambient temperature.

Copper iodate crystals cannot be crystallized by high temperature methods, as 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, moreover, this method is simple and inexpensive. Hence the crystals of copper iodate were grown by gel method.

The present chapter 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 chapter also predicts the results obtained from the different techniques used for the characterization of gel grown crystals of copper iodate.

II. METHODS AND MATERIALS

A. 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 chloride or copper nitrate solution was added with constant stirring in mixture of acetic acid and sodium Meta silicate solution. Continuous stirring process avoids excessive ion concentration which otherwise causes premature local gelling and makes the final medium inhomogeneous and turbid. The pH of the mixture was maintained at 4.4, 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.

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 10-13days. The completely set gel was left for aging for 4days. i.e., 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.

The chemical reaction inside the gel can be expressed as

$XCl_2 + 2YIO_3 \rightarrow X(IO_3)_2 + 2YCl$

Where X=Cu and Y=K

B. Result and Discussion

A Figures shows different forms of grown copper iodate crystals inside the test tubes 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, Star Shaped one beautiful (2mm) shinning crystal is observed. In the test tube of Figure3. 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.

The rate of diffusion seems to be uniform in the complete circular area of the test tube. As the circular ring at the bottom of the transparent region in which crystals are observed quite uniform at the same height i.e., rate of diffusion is constant and uniform .5. Again, the region in which crystals are formed is more transparent compared to nitrate solution. The colour of copper iodate crystal grown with copper nitrate reactant is blue. While with copper chloride reactant is faint green as shown in figure 1. Figure 2 and 3 shows optimized star shaped transparent crystals of copper iodate on a graph paper with their scaling.

Fig1: Starshaped Grown crystal in chloride Gel:

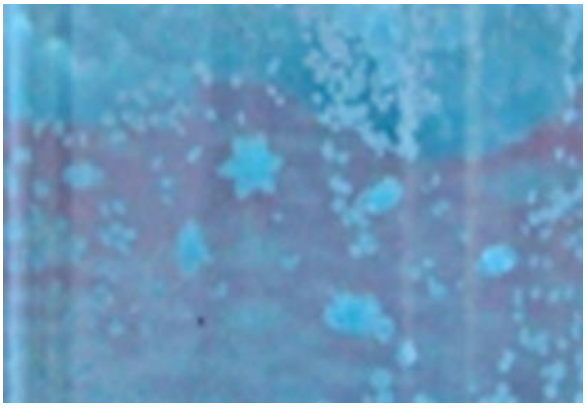


Fig2: Starshaped Grown crystal in Nitrate Gel:

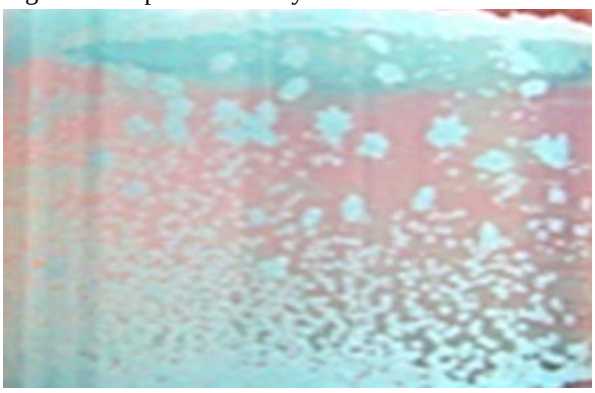
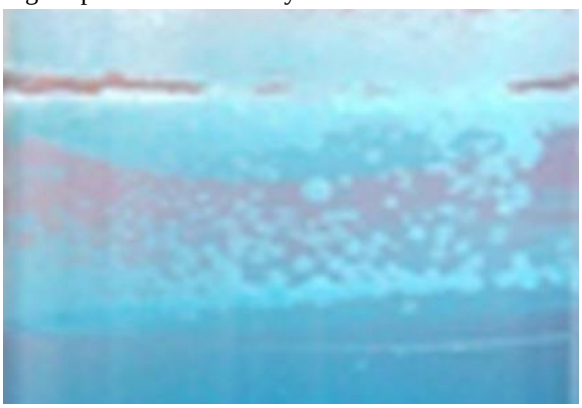


Fig3: Spherulite Grown crystal in Nitrate Gel:



2.1 Effect of various parameters on crystal growth of copper iodate:

It is necessary to study the effect of various parameters in crystal growth of copper iodate. A crystal growth is mainly depends on gel cell size, and cell size is influenced by gel density, gel density depends on pH of gel. Hence, these parameters have profound influence on nucleation density, growth rate habit and quality of crystals. Concentration of reactants and concentration programming has major impact on size habit and morphology of crystals. Hence effect of all these parameters on growth of crystal is discussed as follows.

2.1.1 Effect of gel density:

According to Henish, the proper range of specific gravity of growing good quality crystal is 1.03 to 1.06, by keeping pH constant. The gels of different densities were obtained by mixing sodium Meta silicate solution of specific gravity 1.03 to 1.06 with 2N acetic acid. It is observed that as gel density decreases, transparency of the gel increases. As a rule very dense gels produce poor crystals. On the other hand, gels of insufficient density take long time to form and are mechanically unstable. It is observed that the nucleation density decreases as the gel density increases. Figure 4 shows- the effect of density on number nuclei formed. Fig5 – shows the graph of gel density verses nucleation density. In present work sodium met silicate solution specific gravity 1.04 gm/cc and acetic acid (2N) with 4:1 ratio is an ideal combination for gel formation in the present case of copper iodate. The effect of gel density on nucleation density of copper chloride as shown in figure 3.10.

Figure4: Plot of Effect of gel density on setting time

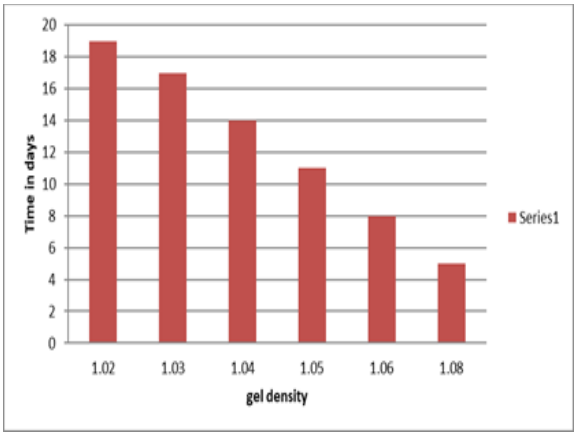
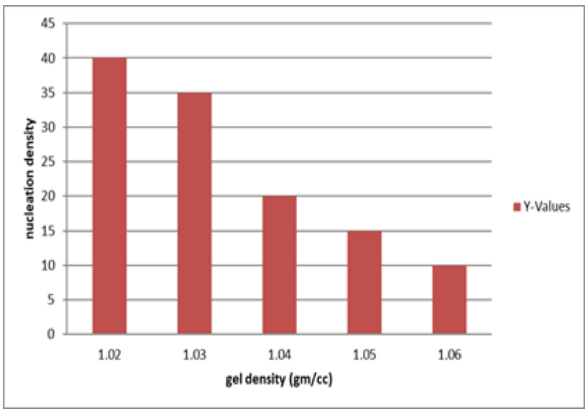


Figure 5: Plot of Effect of gel density on nucleation density



Effect of pH on gel:

This is one of the effective parameters of crystal growth. A value of pH directly effects 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 [139].

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 and the quality of grown crystal is as shown in Table 3.11. The optimum value of gel pH to get ideal gel is found to be 4.4. 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 3.11 shows the graph of pH values against the setting time in hours.

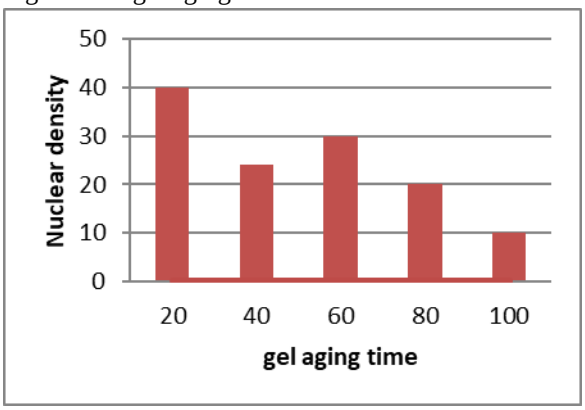
In the present work, pH value of 4.4 is the optimum condition for the good quality crystal of copper iodate. s said, to insert images in Word, position the cursor at the insertion point and either use Insert | Picture | From File or copy the image to the Windows clipboard and then Edit | Paste Special | Picture (with ―Float over text‖ unchecked).

III. EFFECT OF GEL AGING

Effect of gel aging:

Gel aging is one of the effective parameters 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 framework. 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, thereby decreasing the number of nucleation sites. After the gel containing copper chloride is set, the evaporation of water causes not only the lack of ionic carriers in the channel of gel framework, but also discontinuities in the channel due to the shrinkage of gel. Both these effects would adversely affect the diffusion of reactants ions hence the decrease in the number of nucleation sites. Figure6 shows the effect of aging time on number and the quality of crystal shows graph of aging in hours verses in number of crystals. In the present work aging of 124 hours was found most suitable at ambient temperature.

Figure 6: A gel aging time on number of nucleation



IV. UNITS

4.1 Effect of concentration of reactants:

The effect of concentration of feed solution can be investigated by preparing the gel of the same pH 4.4. Feed solution of either KIO_3, $CuCl_2$ and Cu $(No_3)_2$ were tried. Potassium iodate solutions of concentrations 0.1M to 0.4M molarity were prepared. It was observed that as the concentration of the reactant in the gel increases, the nucleation density also increases.

This may be due to the more effect of Cu ions in the gel. For the growth of good quality crystal of copper iodate, suitable concentration of reactant incorporated in gel is found to be 0.5M. Number of experiments were performed with interchanging the position of reactants.

It is to mention that the reactant [0.5M of $CuCl_2$ and Cu $(No_3)_2$,0.4M for KIO_3] were taken to grow good quality crystal of copper iodate using copper nitrate and copper chloride. Change in the position of reactants does not affect either the quality of the crystal or the number of nucleation centers. However, the use of KIO_3 and $CuCl_2$ yields the better and transparent quality of crystal, in terms of size and shape. Therefore, after getting the optimized condition, all experiment were carried out by incorporating 5cc,1M $CuCl_2$ solution in gel and 15cc,0.4M of KIO_3 solution as supernatant was put over the set gel acidified with 2N acetic acid as a feed solution. Table 3.6 summarizes effect of concentration of reactant on quality, habit, and size of crystal.

4.2 Effect of Concentration programming:

Concentration programming is useful to improve the quality of crystal at the time of growing process, many attempts and trials are performed to obtain optimum condition to grow good quality crystal of copper iodate. In present work feed solution of KIO_3 of different concentration ranging from 0.1M to 0.4M were prepared. Over the acetic acid set and aged gel, supernatant KIO_3 solution was added. This feed solution was replaced by another dual volumes feed solution in next 24 hour. The strength feed solution was increased in steps of 0.1 M. The process was continued until the concentration of KIO_3 reached 0.4 M. It was found that with very dilute reactant, the amount of material diffused through the gel is very small. Hence, the rate at which super saturation is attained is low. Under these circumstances, very few nuclei are formed. On increasing the concentration of feed solution, number of nucleation centers was found to increase rather than the growth of already existing nuclei. Hence, it has been observed that the concentration programming is neither helpful for reducing the nucleation density nor it improves the

size and quality of crystal. Finally, quality and transparency of copper iodate crystal were increased due to the increase in concentration of Feed solution or supernatant of KIO_3 to some extent.

Colour:
It is observed that an acidified gel containing copper nitrate leads to growth of blue colour crystal of copper iodate, while gel containing $CuCl_2$ leads to blue shinning and starshaped required crystal.

V. FIGURES AND TABLES

I. Lattice Parameters:

Condition Lattice parameter	Copper iodate concentrations
Density of sodium Meta silicate	1.04kg/m^3
pH of mixture	4.4
Amount of 2N acetic acid	5ml
temperature	Room temperature
Gel setting time	13 days
Gel aging time	5 days
Concentration of KIO_3	0.4M
Concentration of $CuCl_2$	1M
Concentration of Cu $(NO_3)_2$	1M
Period of growth	4 weeks

VII. CONCLUSION

1. Star shaped copper iodate crystal can be grown by simple gel technique.
2. The effect of pH, concentration of reactants, gel aging and setting, gel density and room temperature is important to grown crystals.
3. It is observed that the colour of copper nitrate is dark blue as compare to copper chloride, copper chloride crystals are shining and transparent, but both are star shaped.
4. Single diffusion gel growth technique is suitable to grow copper iodate crystals.
5. Different habits of copper iodate crystals can be obtained by changing parameter like gel density, its pH, gel aging and gel concentration of reactants etc.
6. Unit cell parameter value and d values closely match with the reported ones.
7. The structure of copper iodate is monoclinic.

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