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Synthesis and Study of Growth Parameters of Zinc Iodate Crystals Grown by Gel Method

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ABSTRACT

In the present investigation, crystals of Zinc iodate, were grown by gel method. Since the compound decomposes before its melting point, conventional high temperature methods for its growth are not suitable. It is sparingly soluble in water; hence, gel method is only the alternative technique for growing 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 zinc iodate [$Zn(IO_3)_2$] have been grown in sodium meta silicate gel using the single diffusion method at room temperature. This research paper involves the growth of the zinc iodate crystals and its study using various parameters such as pH of the gel solution, gel concentration, gel setting time, concentrations of reactants etc. The effect of these parameters on the growth of the crystals has been studied.

Keywords: Gel technique, single diffusion method, zinc iodate crystals, gel density, pH of gel, gel aging, concentration of reactants.

I. INTRODUCTION

Zinc iodate crystals exists in two forms.

- Anhydrous Zinc iodate: $Zn(IO_3)_2$.
- Zinc iodate dihydrate: $Zn(IO_3)_2.2H_2O$.

Generally, all forms of these crystals are synthesized in the laboratory.
The structure of zinc iodate as reported is as shown in the figure-1.

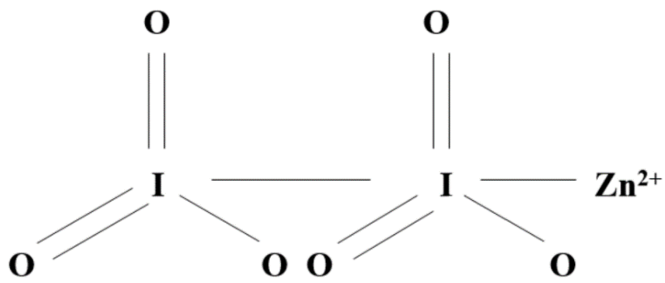

Figure-1: Structure of zinc iodate

The zinc iodates $Zn(IO_3)_2.2H_2O$ and $Zn(IO_3)_2$ were studied jointly by Peter S.; Lange N.; Lutz H. D.; Pracht G. Peter S.; Lange N.; Lutz HD.; Pracht G.

using X-ray, IR-and Raman spectroscopic methods. The crystal structure of the dihydrate, which is isostructural with the respective cobalt compound, was determined by X-ray single-crystal studies (space group $P\bar{1}$, a = 490,60, b = 667.31, c = 1088.85 pm, alpha = 98.855º, beta = 91.119º, and gamma = 92.841º). Transconfigurated $Zn(IO_3)_2.H_2O$ octahedra are three dimensionally connected via common IO_3-ions parallel to [001] and hydrogen bonds parallel to [100] and [010], respectively. Anhydrous $Zn(IO_3)_2$ crystallizes in space group P2 (Z = 2) with a = 548.9), b = 512.4, c = 941.8 pm, and beta = 90.5 degrees. The structure of $Zn(IO_3)_2$ is a monoclinically distorted. The infrared and Raman spectra as well as a group theoretical treatment are presented and discussed with respect to mutual exclusion principle (possible space groups), the strength of the hydrogen bonds and the distortion of the IO_3-ions at the C-1 lattice sites.

II. METHODS AND MATERIAL

The growth of zinc iodate crystals in gel media was achieved by using the single diffusion method. Apparatus used for performing the experiments were borosil glass test tubes of 25cm in height and 2.5cm in diameter, a magnetic stirrer, pH meter, burettes and pipettes, beakers and specific gravity bottle etc.

A gel was prepared by using various concentrations of acetic acid and sodium meta silicate. For this purpose, 5cc, 2N acetic acid was taken in a beaker, to which sodium meta silicate solution having different densities was added drop by drop with the help of burette. During this procedure the solution was continuously stirred by means of magnetic stirrer so as to avoid premature local gelling. Then 5cc zinc chloride solutions 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. Experiments were carried out to optimize 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 12 days for setting. This set gel was allowed to age for 3 days. Aging helps to control the nucleation caused due to reduction in the diameter of the capillaries in gel. Potassium or sodium iodate was used as supernatant. Supernatants having different molarities were carefully poured over the set gels. Experiments were also carried out by interchanging positions of the reactants.

The chemical reaction inside the gel can be expressed as

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

Where X = Zn and Y = K or Na

III. RESULTS AND DISCUSSION

It was observed that nucleation takes place after 7 to 8 days on the surface of the gel and supernatant solution and rarely inside the gel. Number of nuclei produced is inversely proportional to the distance from the gel interface. The number of nuclei decreases as we go away from the gel interface. Formation of nuclei depends upon number of parameters such as pH, density of gel, aging period and concentration of reactants.

In the steady state of concentration gradient, growth rate also becomes steady which favors growth of well developed crystals.

During the growth process, there was sudden decrease in the temperature of the atmosphere. Because of this decrease in room temperature, there was reduction in the solubility of supernatant KIO3. Also the rate of formation of the bi product KCl in a test tube containing high concentration of Zinc chloride was more. As a result the precipitate of the bi product KCl formed above the interface of the gel was some what at the control rate. The bi product KCl was white and opaque. In this way the whisker (thread like) growth of bi product KCl was observed over the interface of the gel and in the supernatant present above gel in the test tube. These whiskers so formed were pointed in the upward direction in the supernatant instead of whiskers pointing in the downward direction in the gel. Such phenomenon has not been observed so far in this laboratory. It was unusual phenomenon.

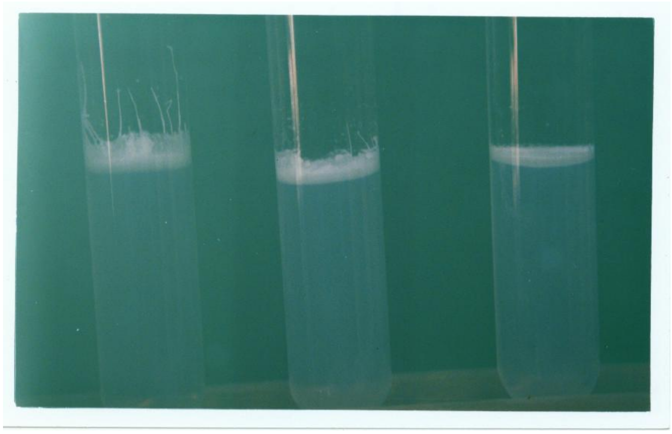

Figure-2 : Unusual phenomenon

This phenomenon was mostly attributed to sudden decrease in the room temperature because of the cold season. This unusual phenomenon for different concentrations 0.5M, 1M and 1.5M of Zncl2 respectively is as shown in the figure-2.

Then whiskers of the bi product were removed gently and again fresh supernatant KIO3 was incorporated over the gel in each test tube.

Large numbers of micro crystals were obtained near the gel interface. Hexagonal crystals of appreciable size little away from the gel interface and star shaped crystals of smaller size far away from the gel interface were obtained. It was observed that the number of crystals growing diminished with the increase in the distance from the gel interface. It may be due to the reduced rate of diffusion of supernatant. Second reason may be attributed to the gel aging, since the crystals in this region nucleate in a comparatively older gel.

The number of nucleation centers and growth rate decreases with increase in aging of gel. Insufficient gel aging often causes the fracturing of gel at the time of incorporating the supernatant. High concentration of reactants results in to formation of a thick layer created by large number of micro crystals attached themselves at the interface. This may be happened due to high diffusion gradient near the gel interface. Less concentration of reactants leads to the formation of star shaped crystals due to slow diffusion rate and insufficient supply of reactants.

Fig-3: Growth of zinc iodate crystals

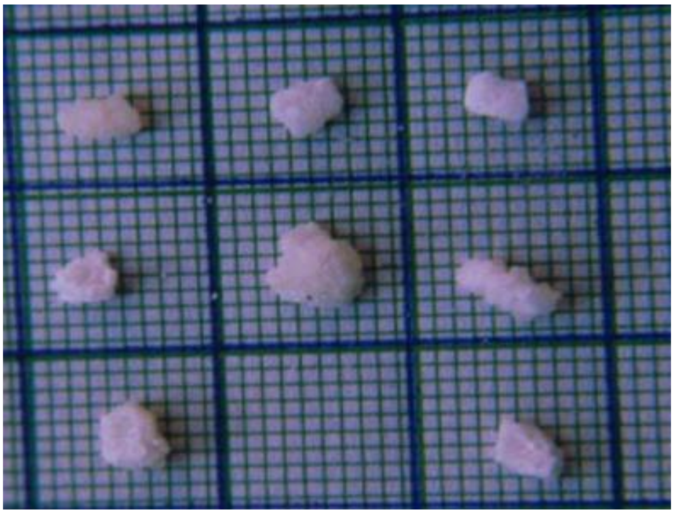

Fig-4: Few transparent crystals of zinc iodate.

Fig.-3 shows the optimized crystals of zinc iodate grown near the gel interface inside the test tube. The shape of these crystals appeared to be hexagonal on higher magnification. These crystals were opaque at the centre but appeared to be transparent at the edges. The large sized crystals were grown. Fig-4 shows few crystals of zinc iodate having different habits on a graph paper with their scaling.

Effect of various parameters on crystal growth :

The effect of various parameters on the crystal growth rate necessarily studied. The crystal growth rate mainly depends on gel cell size, gel density, gel age and pH of the gel etc. 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, morphology and habit of crystals. Hence, effect of all these parameters on growth of crystals is discussed in the following sections with respect to the results obtained.

Effect of gel density :

The proper range of specific gravity to grow good quality crystals is 1.03 to 1.06, according to Henisch. The gels of different densities were obtained by mixing sodium meta silicate of specific gravity 1.03 to 1.06 with 2N acetic acid, keeping pH value constant. It was observed that transparency of the gel increases with decrease of the gel density. As a rule, very dense gels produce poor crystals. On the other hand, gels of lower density take long time to set and are mechanically unstable. It is observed that the nucleation density decreases with increase of gel density. Table-1 shows the effect of gel density on number of nuclei formed. The graph of gel density against nucleation density is as shown in the fig.-5. Sodium meta silicate solution of 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.

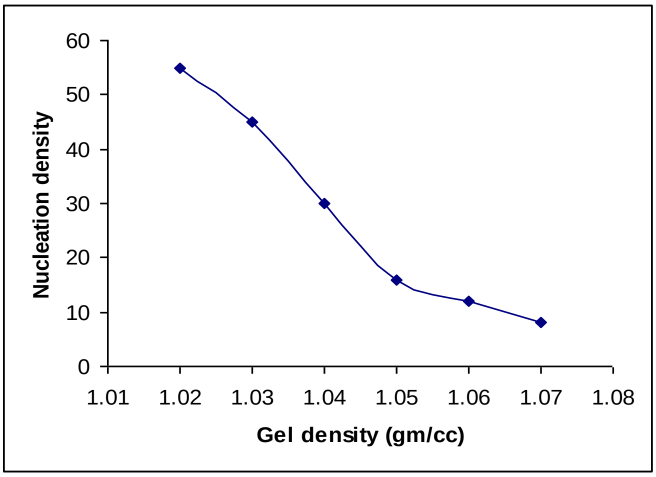

Figure 5: Plot of gel density against nucleation density

Table-1: Effect of gel density on nucleation density (pH = 4.4, feed solution 0.4M KIO_3)

Test tube No.	Acetic acid 2N (cc)	$ZnCl_2$ incorporated in gel 1.0M (cc)	Density of gel (gm/cc)	Number of nuclei formed	Observations
1	5	5	1.02	55	Large number of micro crystals were formed near the gel interface. Their shape was not identified.
2	5	5	1.03	45	Large number of micro crystals were produced. They were attached themselves and formed a thick layer at the gel interface. Their shape was not identified.
					Large number of micro crystals

3	5	5	1.04	30	were produced. They were attached themselves and formed a thick layer at the gel interface. However some crystals were well isolated and their shape was noticed.
4	5	5	1.05	16	Crystals at the gel interface are very close together.
5	5	5	1.06	12	Grains of crystals formed by the number of crystals of irregular shape were observed.
6	5	5	1.07	8	Few small opaque crystals of indefinite shape were observed.

Effect of pH of gel :

It is known that initial pH value of the gel does not indicate the acidity of the gel after gelation. Even then, these pH values will have a profound effect on the gel structure, nucleation and growth of the crystal as observed during the present investigation. Experiments were repeated by keeping the amount of one of the reactants say supernatant KIO_3 or $NaIO_3$ over the set gel constant. The pH of the gel was changed by varying the composition of acetic acid, sodium meta silicate and another reactant $Zncl_2$. The effect of pH on growth rate was studied.

Table-2 : Effect of pH on gel (Aging period = 5 days, feed solution 0.4M KIO_3)

Test tube No.	**Acetic acid 2N (cc)**	**$ZnCl_2$ incorporated in gel 1.0M (cc)**	**Sodium meta silicate 1.04 (gm/cc)**	**pH of mixture**	**Gel Setting Time (days)**	**Observations**
1	5	5	15.5	2.0	-	Gel is not set
2	5	5	17.0	2.5	-	Gel is not set
3	5	5	18.2	3.0	-	Gel still loose after 1 month
4	5	5	18.8	3.5	15	Few crystals of smaller size near the gel interface.
5	5	5	19.3	4.0	13	More number of micro crystals of smaller size near the gel interface.
						The crystals were transparent, well isolated

6	5	5	20.1	4.4	12	and their shape was hexagonal.
7	5	5	20.6	4.5	10	Large number of micro crystals, opaque and having indefinite shape
8	5	5	21.4	5.0	7	A thick layer of micro crystals near the gel interface.
9	5	5	21.6	5.5	4	Large number of micro crystals gathered together near gel interface, opaque and star shaped.
10	5	5	22.0	6.0	2	Few micro crystals
11	5	5	22.3	6.5	1	Number of micro crystals bunched together
12	5	5	22.5	7.0	Immediate setting	Very less no. of crystals

The effect of different pH values on gel setting time and the quality of crystals grown is as shown in the table-2. To get an ideal gel, the optimum value of gel pH is found to be 4.4. For the pH values less than 4.4, the gel setting time increases and the resultant gel was unstable, and for pH values greater than 4.4, the gelation occurred very soon and the resultant gel was not transparent.

Initial pH value may not remain constant after gelation, but still it has profound effect on gel structure, the nucleation and growth of crystals.

In the present work, pH value of 4.4 is the optimum condition for the growth of good quality crystals.

Effect of gel aging :

The effect of gel aging can be studied by allowing the gels of same pH and density to age for various periods. Supernatant of constant molarity was then added as a feed solution over the set gel. It was found that the number of zinc iodate crystals decreases with increases in aging of gel. Aging of gel decreases the pore size as well as 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

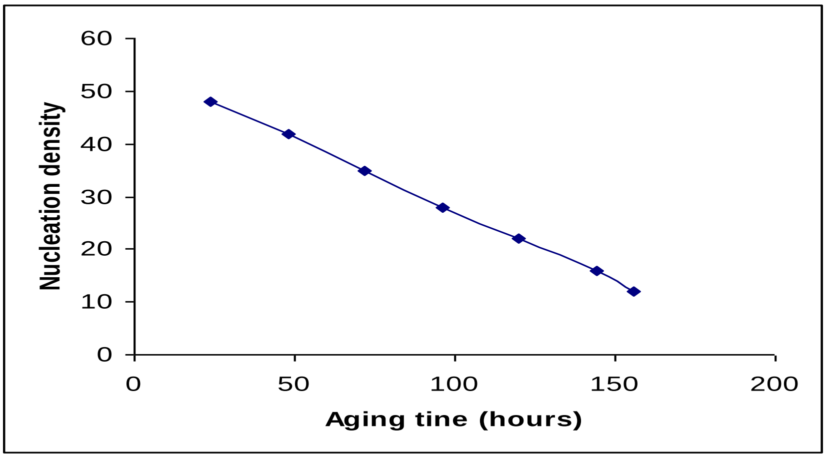

Figure-6 : Plot of gel aging time against nucleation density

Table-3: Effect of gel aging time (pH = 4.4, feed solution 0.4M KIO_3)

Test tube No.	Acetic acid 2N (cc)	$ZnCl_2$ incorporated in gel 1.0M (cc)	Sodium meta silicate 1.04 (gm/cc)	Aging time (hours)	Number Of crystals	Observations
1	5	5	20	24	48	High nucleation density, few micro crystals
2	5	5	20	48	42	High nucleation density more micro crystals
3	5	5	20	72	35	Low nucleation, few crystals near gel interface
4	5	5	20	96	28	Low nucleation, few opaque and star shaped crystals
5	5	5	20	120	22	Hexagonal and transparent crystals near gel interface
6	5	5	20	144	16	Low nucleation density, few opaque crystals
7	5	5	20	156	12	Low nucleation density, very few crystals

decreases the diffusivity of potassium or sodium ions in the gel, thereby decreasing the number of nucleation sites. After the gel is set, the evaporation of water causes not only the lack of ionic carriers in 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 K^+ or Na^+ ions hence the observed decrease in the number of nucleation sites. The effect of aging time on number and the quality of crystals is listed in the table-3. A graph of aging time in hours against the number of crystals is as shown in the figure-6.

In the present work, aging of 120 hours was found suitable because it makes the gel neither dry or brittle nor fragile. The aim of reduction in nucleation centers can also be achieved. Hence aging period of 120 hours is the optimum condition for the growth of good quality crystals.

Effect of concentration of reactants :

The effects of concentration of feed solutions can be investigated by preparing the gel of the same pH and density. Feed solutions of either KIO_3 or $NaIO_3$ and $ZnCl_2$ were tried. KIO_3 and $NaIO_3$ solutions of 0.1M to 0.4M molarity were prepared. By keeping the molarity of the supernatant KIO_3 or $NaIO_3$ over the set gel constant, $ZnCl_2$ of different molarities incorporated in the gel were tried. 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 enhanced availability of Zn^+ ions in the gel. For the growth of good quality crystals, suitable concentrations of reactant incorporated in the gel is found to be 1.0M and for the feed solution (Supernatant) over the set gel, it is found to be 0.4M. Experiments were carried out by interchanging the positions of the reactants i.e. KIO_3 or $NaIO_3$ of specific molarity was incorporated in gel and $ZnCl_2$ as a feed solution of different molarities ranging from 0.5M to 1.5M was put over the set gels.

Table-4 summarizes the effects of concentration of reactants on habit, quality, and size of crystals.

Table-4: Effect concentration of reactants on habit, quality and size of $Zn(IO_3)_2$ crystals

Concentration of reactant in gel	Concentration of reactant above gel	Remarks
$ZnCl_2$ 0.5 M ; 5 ml	KIO_3 or $NaIO_3$ 0.4 M	Large number of micro crystals were produced. They were attached to themselves and form a thick layer of crystals at the interface. Crystals were transparent and shining but there were no diffusion of crystals below interface.
$ZnCl_2$ 1.0 M ; 5 ml	KIO_3 or $NaIO_3$ 0.4 M	Large number of micro crystals were produced. The shape of the crystals appeared to be hexagonal on higher magnification. The crystals were opaque at the centre but transparent at the edges. The large size crystals were grown.
$ZnCl_2$ 1.5 M ; 5 ml	KIO_3 or $NaIO_3$ 0.4 M	Large number of micro crystals produced a thick layer a interface and attached themselves. Crystals were opaque and their shape was not clear. The size of crystals were smaller than previous case.

It has been observed that there are no changes in the values of concentrations of reactants [1.0M for $ZnCl_2$ and 0.4M for KIO_3 or $NaIO_3$] to grow good quality crystals. 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 instead of $NaIO_3$ and use of $ZnCl_2$ instead of $Zn(NO_3)_2$ yields better quality crystals, in terms of size and shape. Therefore, after getting the optimized conditions, all experiments were carried out by incorporating 5cc, 1.0M $ZnCl_2$ solution in gel and 10cc, 0.4M KIO_3 solution (Supernatant) was put over the set gel acidified with 2N acetic acid as a feed solution.

Concentration programming :

Once the optimum growth conditions for concentration of reactants are established, Single diffusion experiments of concentration programming were carried out in order to observe the nucleation control phenomenon. Feed solutions of KIO_3 of different concentrations from 0.1M to 0.4M were prepared. Over the acetic acid set gel, 0.4M KIO_3 solution was slowly added. This feed solution was replaced by another equal volume feed solution in next 48 hours. The strength of feed solution was increased in steps of 0.1M. The process was continued until the concentration of KIO_3 reached 0.4M. It was found that for lower concentration of supernatant, there will be no nucleation. After increasing the concentration, few nuclei were formed. Further increase in concentration created very few nucleation centers and helped the previous nuclei to grow to their optimum size. Slight change in luster and morphology is observed. Hence, it can be said that though it is not much useful, concentration programming is slightly helpful in improving the quality of crystal.

IV. CONCLUSION

From the above studies the following conclusions are drawn :

1. The crystals of zinc iodate can be grown by using gel technique.
2. Single diffusion gel growth technique is suitable for growing zinc iodate crystals.
3. Different habits of zinc iodate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
4. Most suitable value of gel density is found to be 1.04 gm/cc.
5. Aging helps in controlling nucleation rate.
6. The pH value of 4.4 is found to be suitable for growing these crystals

V. REFERENCES

[1]. Dishovsky, N. and Boncheva – Maladenova, Z. J. Crystal Growth 51 (1981) 147.

[2]. Saraf, K. B. Ph.D thesis, Sardar patel University, Vallabh vidya nagar, (1980).

[3]. Dr. P. Santhana Raghavan and Dr. P. Ramaswami, Crystal growth centre, Anna University, Chennai.

[4]. M. Maneva and V. Koleva, Jornal of thermal analysis Volume 42 (1994)

[5]. Nassau, K. Am. Mineralogist 63 (1928) 219.

[6]. Joshi, M. S. and Antony, A. V. J. Mater. Sci. 13 (1978) 939.

[7]. Desai, C. C. and Raman, M. S. V. J. Cryst. Growth 102 (1990) 191.

[8]. Bechhold, H. and Zeigler, K. Ann. Phys. 20 (1906) 900.

[9]. Basset, J.; Denny, R.C.; Jeffery, G. H. and Mendham, J. Vogel's Text Book of Quantitative Inorganic Analysis, 4th Ed. Longman (1982).

[10]. Willard, H. H.; Merrite, J. R., Dean J. A. and settle, F. A. Instrumental Methods of analysis, 6th edition. GGS publication and distribution, New Delhi (1986).

[11]. Shell, F. D. and Biffen, F. M. Chemical methods of anlysis, D. B. Taraporewala Sons and Co., Bombay (1964)

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