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Effect of different parameters on the growth of gel grown strontium iodate crystals

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Abstract
The single crystals of strontium iodate iodate crystals have been grown in sodium meta silicate gel using the single diffusion method at room temperature. This research paper involves the growth of the strontium 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, strontium iodate crystals, gel density, pH of gel, gel aging, concentration of reactants etc

Introduction
Strontium iodate crystals exists in three forms.
- Anhydrous strontium iodate: $Sr(IO_3)_2$.
- Strontium iodate monohydrate: $Sr(IO_3)_2.H_2O$.
- Strontium iodate hexahydrate: $Sr(IO_3)_2.6H_2O$.

Generally, all forms of these crystals are synthesized in the laboratory.
Growth of single crystals of Strontium iodate, Sr(IO3)2, is reported by Xuean Chen, Weiqiang Xiao, Xinan Chang and Hegui Zang. It has been prepared by hydrothermal reactions at 170 °C. The X-ray single-crystal structural analysis showed that it crystallizes in a new structure type with space group $P\bar{1}$, a = 7.0130Å, b = 7.0520Å, c = 13.088Å, α = 84.12°, β = 84.80°, γ = 63.48°. The crystal structure of $Sr(IO_3)_2$ consists of pyramidal IO_3^- anions and Sr^{2+} cations, which are alternately arranged along the a-axis in a 2:1 ratio to form a layer-like structure. Infrared spectra further confirmed that the compound contains low symmetric IO_3^- groups.

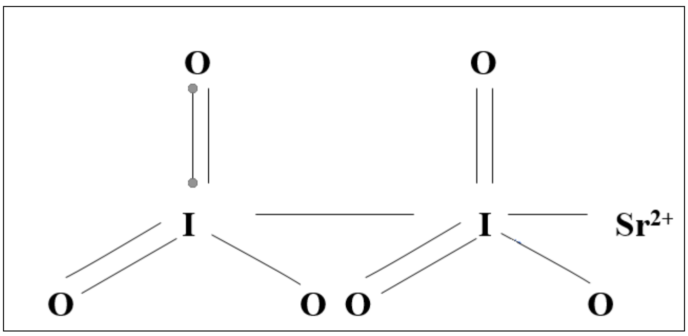

Fig 1: Structure of strontium iodate

The reported structure of strontium iodate is as shown in the figure-1.
Single crystals of strontium iodate grown by gel method are reported by Prof. Dr. M. S. Joshi, S. G. Trivedi. Optimum growth conditions for good quality single crystals are worked out. Different habits of these crystals are reported. Single crystals of Strontium iodate monohydrate $Sr(IO_3)_2.H_2O$ were grown by T. Vogt using interdiffusion of $SrCl_2$ and HIO_3 solutions in an H-shaped tube with an intermediate layer of pure water at room temperature.

Materials and Methods

The aim of the present work is to put the gel method on an anvil and thus to rest its performance and potentiality in producing larger and more perfect crystals. In the present investigation, aqueous solutions of two salts are brought together by diffusion through a silica gel with subsequent nucleation and the crystal growth, which continues due to the gradual precipitation of the insoluble product phase of the reaction. No reaction waste material is formed within the gel.

Strontium 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 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 strontium iodate, monohydrate [$Sr(IO_3)_2 . H_2O$] were grown by gel method. All the chemicals used were of A.R. grade.

Results and Discussion

In the present work, single diffusion method was used. In actual procedure, 5cc, 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 of 4.4. Continuous stirring process avoids excessive ion concentration which otherwise causes premature local gelling and makes the final medium inhomogeneous and turbid. To this mixture, 5cc of strontium chloride or strontium nitrate solution (one of the reactants) was added with constant stirring. The pH of the mixture was maintained at 4.4. Number of experiments were carried out in order to secure appropriate range of pH values which in turn gives a good gel allowing to grow good quality crystals.

Fig 2: Growth of strontium iodate crystals

Figure-2 shows different forms of growth of strontium iodate crystals inside the test tubes.

The chemical reactions inside the gel can be expressed as

$$XCl_2 + 2YIO_3 \rightarrow X(IO_3)_2 + 2YCl \text{ OR } X(NO_3)_2 + 2YIO_3 \rightarrow X(IO_3)_2 + 2YNO_3$$

Where X = Sr and Y = K or Na

Fig 3: Growth forms of strontium iodate crystals inside the test tube

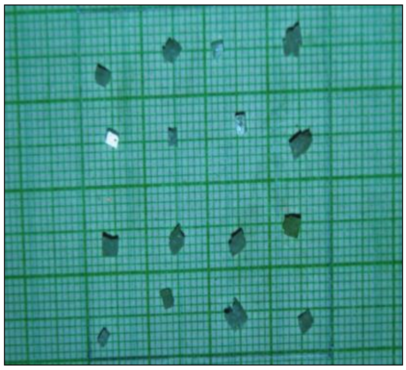

Fig 4: Few cubical transparent crystals of strontium iodate.

Figure-3 shows optimized cubical transparent crystals of strontium iodate near the bottom inside the test tube while Figure-4 shows few cubical transparent crystals of strontium iodate on a graph paper with their scaling.

Effect of gel density

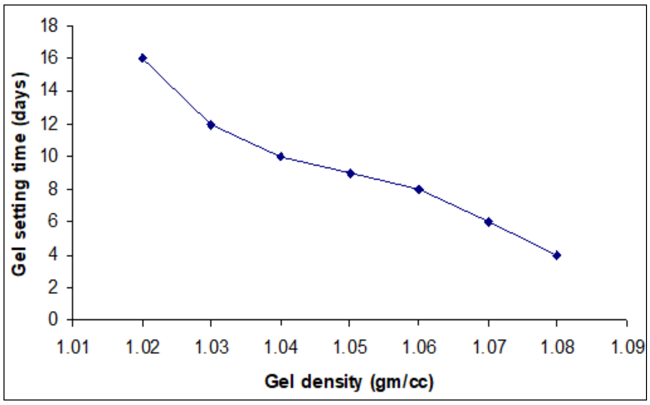

Fig 5: Plot of gel density against gelation time

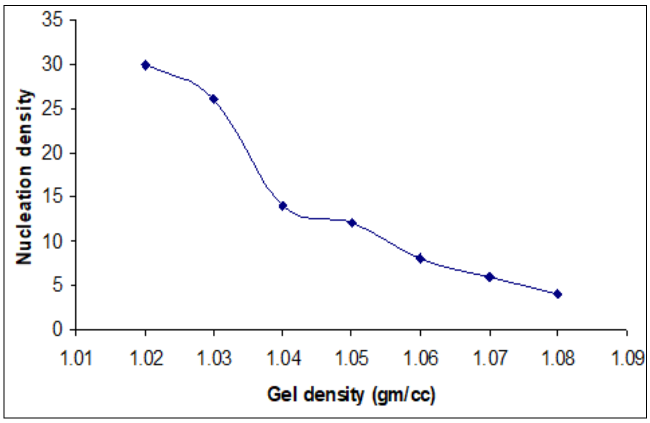

Fig 6: Plot of gel density against nucleation density

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

Test tube No.	Acetic Acid 2N (cc)	$SrCl_2$ incorporated in gel 0.5M (cc)	Density of gel (gm/cc)	Gel setting Time (days)	Observations
1	5	5	1.02	16	Gel is not stable
2	5	5	1.03	12	Gel takes very long time to set and still firmness is not sufficient
3	5	5	1.04	10	Whisker, dendritic and few cubical transparent crystals
4	5	5	1.05	09	Whisker, dendritic and less number of crystals

5	5	5	1.06	08	Number of transparent crystals decreases with increase in whiskers and dendrites
6	5	5	1.07	06	Only whisker and dendritic growth
7	5	5	1.08	04	Only whisker growth

The gels of different densities were obtained by mixing sodium meta silicate solutions of specific gravity 1.02 to 1.08 with 2N acetic acid, keeping pH value constant. It was observed that transparency of the gel decreased with increase of gel density. Gels with higher densities required less gel setting time compared to the gels with lower densities. It may be noted that well-defined and transparent crystals were obtained with sodium meta silicate density 1.04 gm/cc. On the other hand, gels with densities below 1.04 gm/cc required longer time to set and still gels were not stable. Density of 1.02 gm/cc was the lower practical limit. The effect of gel densities on the quality of crystals is listed in a table-1.

Table 2: Effect of gel density on setting time (pH = 4.4, feed solution 0.4M KIO_3)

Test tube No.	Acetic Acid 2N (cc)	$SrCl_2$ incorporated in gel 0.5M (cc)	Density of gel (gm/cc)	Number of nuclei formed	Observations
1	5	5	1.02	30	Whiskers smaller in size, few curved dendrites and more number of small opaque crystals were observed
2	5	5	1.03	26	Whiskers smaller in size, few curved dendrites and less number of big transluscent crystals were observed
3	5	5	1.04	14	Whisker, dendritic and few cubical transparent crystals of appreciable size were observed
4	5	5	1.05	12	Whisker, dendritic and less number of crystals
5	5	5	1.06	08	Longer whiskers but shorter dendrites with few number of slightly transparent crystals were oberved
6	5	5	1.07	06	Only whiskers with less number of few opaque crystals were observed
7	5	5	1.08	04	Only few opaque crystals

Table-2 shows the effect of density on number of nuclei formed.

Figure-5 shows the variation of gelation time with gel density. It is observed that the gelation time decreases with increase in gel density.

The effect of density on number of nuclei formed has been graphically shown in Figure-6. A greater gel density implies smaller pore size and poor communication among the pores and thus decreasing the nucleation density. Bechhold *et al*, showed that diffusion coefficient becomes distinctly smaller as gel densities increased. There is no evidence that the diffusion constant of small atoms and ions is greatly influenced by the silica gel density as long as the density is low. Thus, the diffusion constants are not greatly influenced by the presence of dilute gel.

Effect of pH of gel

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 to 6. It was observed that as pH increased, transparency of the gel decreased. Crystals growing at higher values 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 appears to lack cross-linkages and the cellular nature becomes less distinct. Number of nuclei also decreases and the crystals are not well defined, due to improper formation of cells at high pH values.

Table 3: Effect of pH on gel (Aging period = 5 days, feed solution 0.4M KIO_3)

Test tube No.	Acetic Acid 2N (cc)	$SrCl_2$ incorporated in gel 0.5M (cc)	Sodium meta silicate 1.04 (gm/cc)	pH of mixture	Gel Setting Time (days)	Observations
1	5	5	15.0	2.0	-	Gel is not set
2	5	5	16.5	2.5	-	Gel is not set
3	5	5	17.0	3.0	-	Whiskers of shorter length
4	5	5	18.0	3.5	15	Whiskers of length about 1.5-2.0cm below interface
5	5	5	19.5	4.0	13	Longer whiskers with shorter opaque dendrites
6	5	5	20.0	4.4	12	Whiskers, dendrites and few cubical transparent crystals of appreciable size
7	5	5	20.4	4.5	10	Whiskers, dendrites and more no. of cubical opaque crystals of smaller size
8	5	5	21.5	5.0	7	No. of crystals decreases
9	5	5	21.6	5.5	4	On higher magnification star shaped opaque
10	5	5	22.0	6.0	2	whisker growth with few dendrites
11	5	5	22.3	6.5	1	Only whiskers
12	5	5	22.5	7.0	Immediate setting	Very few whiskers, not well defined

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 different pH values on gel setting time and the quality of crystals grown is as shown in the table-3.

Figure-7 shows the graph of pH values against the setting time in days. Initial pH value may not remain constant after gelatin, 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.

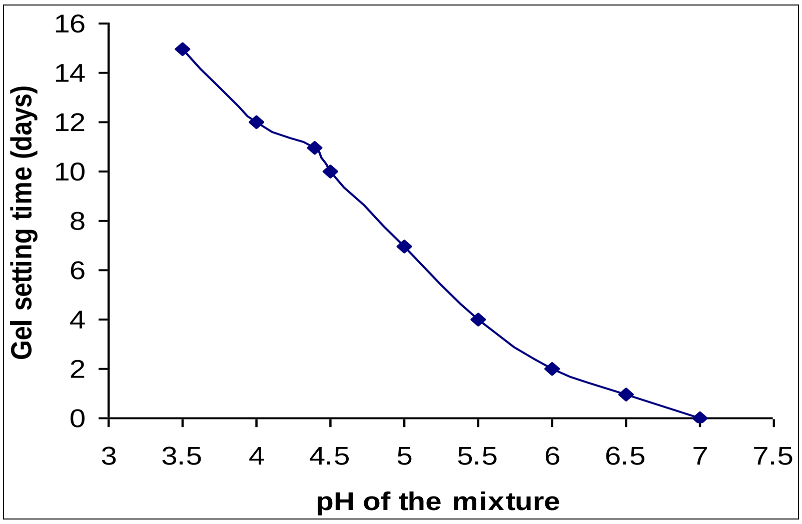

Fig 7: Plot of pH against gel setting time

Effect of gel aging

Gel aging plays an effective role on the growth of crystals as reported by Henisch *et al*. To investigate the effect of aging on gels, gels of same pH and density were allowed to age for various periods before adding the feed solution. It was found that the nucleation density decreases as the aging increases. Aging of gel reduces number of nucleation centers and growth rate. The reason may be the formation additional cross-linkages between siloxane chains with increasing gel age, resulting in a gradually diminishing cell size.

This in turn reduces nucleation centers, since many nuclei find themselves in cells of very small size, where further growth is not possible. Insufficient gel aging leads to the formation of fragile gel and it often breaks at the time of addition of supernatant. The effect of gel aging time on the number and the quality of crystals is as shown in the table-4. Figure-8 shows the graph of aging time in hours against the number of crystals.

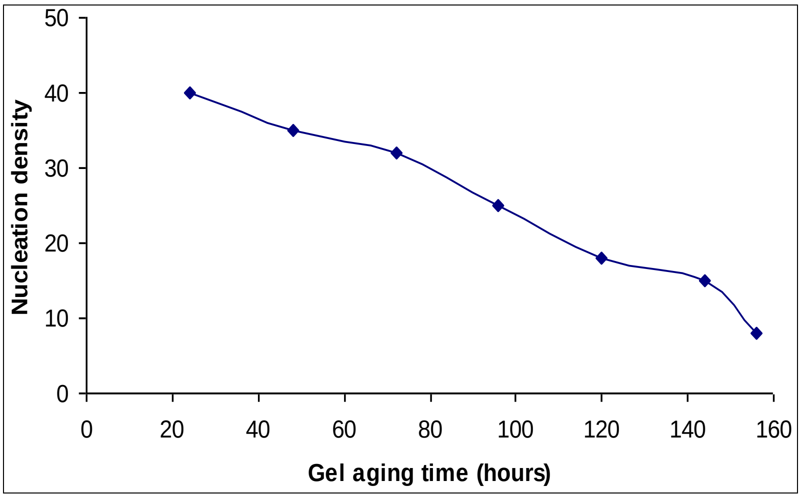

Fig 8: Plot of gel aging time against nucleation density

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.

Table 4: Effect of gel aging time (pH = 4.4, feed solution 0.4M KIO_3)

Test tube No.	Acetic Acid 2N (cc)	$SrCl_2$ incorporated in gel 0.5M (cc)	Sodium meta silicate 1.04 (gm/cc)	Aging Time (hours)	Number Of crystals	Observations
1	5	5	20	24	40	High nucleation, whisker and dendritic growth
2	5	5	20	48	35	High nucleation, whisker and opaque dendritic growth
3	5	5	20	72	32	High nucleation, whisker, dendritic and few opaque crystals
4	5	5	20	96	25	Low nucleation, whisker growth
5	5	5	20	120	18	Whisker, dendritic and few cubical transparent crystals
6	5	5	20	144	15	Low nucleation density, few crystals
7	5	5	20	156	8	Low nucleation density, few 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 $SrCl_2$ or $Sr(NO_3)_2$ were tried. KIO_3 and $NaIO_3$ solutions of 0.1M to 0.4M molarity were prepared.

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 $SrCl_2$ 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, SrCl2 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 Sr^+ ions in the gel. For the growth of good quality crystals, suitable concentrations of reactant incorporated in the gel is found to be 0.5M 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 $SrCl_2$ as a feed solution of different molarities ranging from 0.1M to 0.5M was put over the set gels.

It has been observed that there are no changes in the values of concentrations of reactants [0.5M for $SrCl_2$ or $Sr(NO_3)_2$ 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 $SrCl_2$ instead of $Sr(NO_3)_2$ yields better quality crystals, in terms of size and shape. Therefore, after getting the optimized conditions, all experiments were carried out by incorporating 5cc, 0.5M $SrCl_2$ solution in gel and 0.4M KIO_3 solution (Supernatant) was put over the set gel acidified with 2N acetic acid as a feed solution.

Table-5 summarizes the effects of concentration of reactants on habit, quality, and size of crystals.

Table 5: Effect concentration of reactants on habit, quality and size of $Sr(IO_3)_2$ crystals

Concentration of reactant in gel	Concentration of reactant above gel	Habit	Quality	Size
$SrCl_2$ 0.1 M; 5 ml	KIO_3 0.4 M	Whisker	Opaque, Brittle	4 cm
$SrCl_2$ 0.2 M; 5 ml	KIO_3 0.4 M	Whisker Dendritic	Opaque, Brittle Curved	3.5 cm--
$SrCl_2$ 0.3 M; 5 ml	KIO_3 0.4 M	Whisker dendritic	Opaque, Brittle Curved	3 cm--
$SrCl_2$ 0.4 M; 5 ml	KIO_3 0.4 M	Whisker Dendritic	Opaque, Brittle Curved	2 cm--
$SrCl_2$ 0.5 M; 5 ml	KIO_3 0.4 M	Whisker Dendritic Cubical	Opaque, Brittle Curved Good	4 cm--$(2 \times 2 \times 2)$ mm^3

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 and aged gel, supernatant KIO_3 solution was 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 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 concentration programming is neither helpful for reducing the nucleation density nor it improves the size and quality of crystal.

Conclusion

1. Gel growth technique is suitable for growing the crystals of strontium iodate.
2. Single diffusion method is convenient for the growth of the strontium iodate crystals.
3. Different habits of strontium iodate crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
4. Some crystals are shining and quite transparent, hence are of reasonably good quality.

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