EFFECT OF GEL PARAMETERS ON THE GROWTH AND NUCLEATION OF LEAD IODATE CRYSTALS

K. D. Girase

S.V.S.'s Dadasaheb Rawal College, Dondaicha, 425408, India.
kdgirase_1964@rediffmail.com

ABSTRACT

In the present investigation, lead iodate crystals were grown in silica gel at ambient temperature. The effect of various parameters like gel concentration, pH of gel, gel ageing, concentration of the reactants on the growth of these crystals were studied. Good quality crystals having different morphologies and habits were obtained. Some of These crystals were opaque and some were translucent.

KEYWORDS

Gel pH, gel density, ageing, concentration of reactants

1. INTRODUCTION

The subject of crystal growth has held a high level of interest, both scientifically and technologically, for a very long period. Nearly all basic solid materials of modern technology are made up of crystals. Hence an understanding of how crystals are grown is an important aspect of the science of materials. The need of better quality crystals in industries and technology cannot be met with from the diminishing natural sources.

In recent years, very few attempts have been made to study growth and characterization of iodate crystals in general. In the literature, there are no reports on the growth and characterization of lead iodate crystals. Most of the iodates exhibit prominent non-linear optics (NLO) behavior. NLO materials exhibiting second harmonic generation and find wide range of applications in the field of telecommunication for efficient signal processing and optical information storage devices. The search for new materials with high optical nonlinearities is an important task. Hence, considering these aspects, growth of lead iodate crystal is very interesting in view of crystallographic and optical properties.

We report here the several aspects regarding the growth procedure of lead iodate; optimum growth conditions and the growth kinetics i.e. influence of different growth parameters to obtain optimization conditions for the growth of these crystals.

2. EXPERIMENTAL

In the present work, single diffusion method was used [1-10]. In actual procedure, 7 cc, 1N acetic acid was taken in a small beaker, to which SMS solution of density 1.04 gm/cc was added drop by drop with constant stirring by using magnetic stirrer, till the pH value 4.2 was set for the mixture. A digital pocket sized pH meter of HANNA instruments was used for this purpose. Continuous stirring process avoids excessive local ion concentration which otherwise causes premature local gelling and makes the final solution inhomogeneous and turbid. To this mixture,

DOI: 10.5121/ijci.2013.2406

5 cc aqueous solution of 0.1 M $Pb(NO_3)_2$ (as inner reagents) was added with constant stirring. The pH of the mixture was maintained at 4.2. Number of experiments were carried out in order to secure appropriate range of pH values which in turn gives a good gel allowing growing a good quality crystals. It was observed that, for the mixture having pH value less than 4.2, gelation takes quite large time of the order of several days. However, in the pH range 4.0 - 4.5, there was appropriate waiting in gellation time. The gel setting time required for the gel solutions having pH value greater than 4.5 was short.

Borosil glass test tubes of diameter 2.5 cm and height 15 cm were used as crystallizing vessels. Above mixture was then transferred to the clean test tube and kept undisturbed for gellation. The mouth of test tube was covered by cotton plug to avoid contamination of the exposed surface with atmospheric impurities and to keep the gel at atmospheric conditions. Initially the mixture appeared to be quite translucent. However, with the lapse of time, its color changed and became milky white when the gel was completely set. The setting time of gel was about 5 days. The set gel was left for 2 more days for ageing. The ageing of the gel reduces the diameter of the capillaries in gel so that the speed of the reaction is automatically controlled. The outer reagent (supernatant), an aqueous solution of 0.1 M KIO_3 was carefully poured along the walls of the test tube with the help of pipette over the set gel in order to avoid breaking of gel surface and internal structure. The nucleation starts as the anions of potassium iodate slowly diffused into the gel column containing lead nitrate and react together to form the expected crystals. The fully grown crystals are shown in Figure 1 Then these crystals were removed from the crystallizing tube and washed in distilled water.

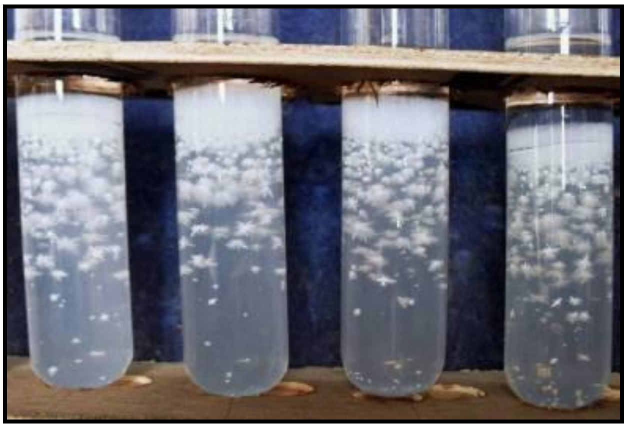

Figure 1 Growth of lead iodate crystals inside the test tubes

(a) **(b)**

Figure 2 Lead iodate crystals outside the test tubes (a) fractal dendrite aggregate crystals and (b) spiky sperulitic and platelets crystals

Figure 2a shows few colorless fractal dendrite aggregate crystals of lead iodate of size 6 x 6 mm on a graph paper with their scaling. Small spiky sperulitic and platelets crystals as shown in Figure 2b were observed for higher concentration of reactants. Experiments were also carried out by interchanging positions of the reactants. All experiments leading to the growth of crystals were carried out at room temperature. In the present investigation, the growth of lead iodate occurs in four different forms viz. spiky spherulites, dendrite (fractal with center), crystal aggregates and platelets. A white precipitate layer of thickness about 0.5 to 1.0 cm was formed at the gel solution interface at the instant of pouring the upper reactant. It may be due to the concentration gradient is very high just below the gel interface and hence the growth rate is very high. Thickness of the precipitation increases with the concentration of upper reactant. The precipitation formed was actually spurious nucleation. Just below the white precipitate there are large number of small sized spiky spherulitic crystals were grown as shown in Figure 3.

As we go below away from the gel interface, the concentration gradient goes on decreasing and hence the growth rate is also goes on decreasing. So at the middle of the test tube multi-branched tree-like (fractal with center) dendrite aggregate crystals were obtained. Figure 4 shows magnified view of multi-branched tree-like (fractal with center) dendrite aggregates crystals.

Figure 3 Magnified view of spiky spherulites crystals of lead iodate

Figure 4 Magnified view of multi-branching tree-like form (fractal with center) dendrite crystals of lead iodate

3. RESULTS AND DISCUSSION

3.1 Optimum condition

Optimum growth conditions for good quality, size and nucleation control of lead iodate crystals is achieved by changing a variety of gel parameters viz. concentration of supernatant (feed solution), gel density, pH of the gel, gel ageing and concentration programming etc. The effect of different gel parameters is discussed in the following sections with respect to the results obtained.

3.2.1 Effect of gel density

The gels of different densities were obtained by mixing sodium metasilicate solutions of specific gravity 1.02 to 1.06 gm/cc with 1N acetic acid, keeping pH value constant.

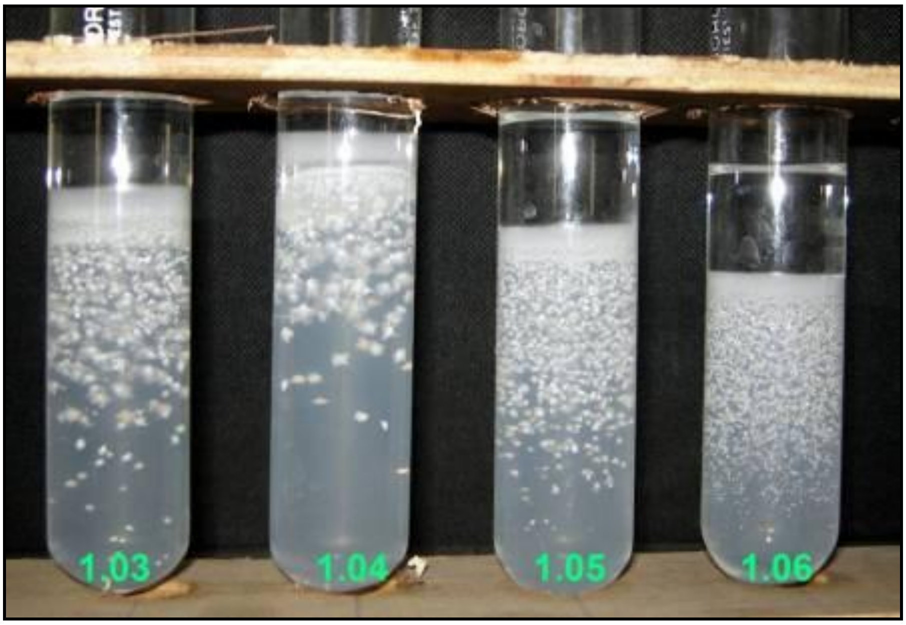

Figure 5 Growth of crystals for different gel densities

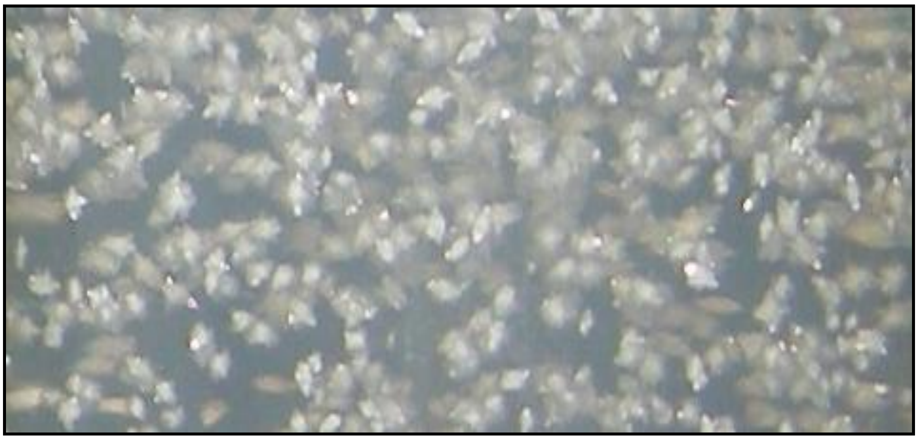

Figure 6 Plate-like crystal habit

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 good size, well defined crystals were obtained with sodium meta silicate with density 1.04 gm/cc. Growth of crystals for different gel densities is shown in Figure 5. A greater gel density implies smaller pores size and poor communication among the pores and thus decreasing the nucleation density. Contradictory to this low nucleation were found in low density gel as shown in Figure 5 It may be due to the fact that at low densities, initially nucleation density is very high hence miniature nuclei are very close each other and adsorption phenomena come into play. Due to this small nuclei get adsorbed to relatively large nuclei. Thus small nuclei are depleted from the nearby region. This results in the formation of crystal aggregates. In present work, Fractal dendrite habit, crystal aggregates were obtained at low gel density 1.03 gm/cc and 1.04 gm/cc while plate-like habit crystals were obtained at high gel density 1.05 gm/cc and 1.06 gm/cc as shown in Figure 6.

In the present work, gel density of the value 1.04 gm/cc is the optimum condition for the growth of good quality crystals.

3.2.2 Effect of pH of gel

By changing the pH of gel with keeping gel composition and concentration of reactants constant, the effect of pH on growth rate was studied. The pH value of gel was varied from 3.5 to 6. It was observed that as pH increased, transparency of the gel decreased. Crystals growing at higher values were not translucent 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.

Gel takes longer time to set with smaller pH values. Such gel can be easily fractured at the time of addition of supernatant.

3.2.3 Effect of gel ageing

Gel ageing plays an effective role on the growth of crystals. To investigate the effect of ageing of 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 ageing increases. Ageing 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 ageing leads to the formation of fragile gel and it often breaks at the time of addition of supernatant. In the present work, it was found that ageing of 48 hours is suitable because it makes the gel neither dry or brittle nor fragile.

3.2.4 Effect of concentration of reactants

The effects of different concentrations of feed solutions can be investigated by preparing the gel of the same pH (4.2) and density (1.04 gm/cc). Feed solutions of either KIO_3 or $Pb(NO_3)_2$ were tried. Initially KIO_3 solution of 0.1 M to 0.4M molarities were used as feed solution and keeping the molarity of the $Pb(NO_3)_2$ constant. Then $Pb(NO_3)_2$ solution of 0.1 M to 0.5 M molarities were used as feed solution and keeping the molarity of the KIO_3 constant.

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 Pb^+ ions in the gel. For the growth of good quality crystals, suitable concentrations of reactant ($Pb(NO_3)_2$) incorporated in the gel was found to be 0.1M and for the feed solution (KIO_3) over the set gel, it was found to be 0.1M.

It has been observed that change in the position of reactants does not affect either the quality of the crystal or the number of nucleation centers. Therefore, after getting the optimized conditions, all experiments were carried out by incorporating 5cc, 0.1 M $Pb(NO_3)_2$ solution in gel and 0.1 M KIO_3 feed solution (Supernatant) was put over the set gel. The growth of lead iodate crystals for different concentrations of reactant is shown in Figure 7.

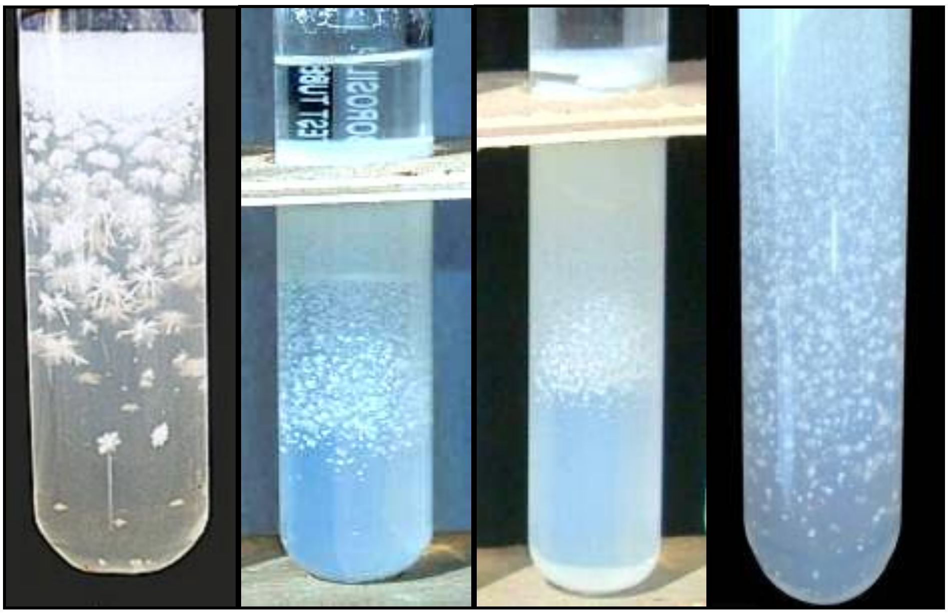

Figure 7 Growth of lead iodate crystals for different concentrations of reactants

Table 1 Optimum conditions for growth of $Pb(IO_3)_2$ crystals

Parameters	**Optimum Condition**
Density of sodium meta silicate solution	1.04 gm/cc
Volume of sodium meta silicate solution	17.5 cc
Volume of 1N acetic acid	7 cc
pH of the gel	4.2
Concentration of KIO_3	0.1 M
Volume of KIO_3	10 cc
Concentration of $Pb(NO_3)_2$	0.1 M

Volume of $Pb(NO_3)_2$	5 cc
Gel setting time	5 days
Gel ageing time	2 days
Period of growth	3 weeks
Temperature	Room Temp.

4. CONCLUSIONS

In view of the above observations, we may conclude the following;

The gel growth system can be successfully used for the growth of lead iodate crystals. Nucleation control can be achieved by changing a variety of gel parameters such as pH of gel, density of gel, ageing of gel and concentration of feed solutions. It was found that crystals having a range of morphologies and habits i.e. translucent, prismatic, shinning, aggregates, spiky sperulitic and multi arm dendrite good quality colorless crystals were obtained.

Acknowledgements

We acknowledge the expertise and help provided by Dr. L. A. Patil, Head, Department of Physics, Pratap College, Amalner for laboratory facilities. One of the authors (KDG) thankful to University Grant Commission (Pune) for financial assistance and Dr. N.O. Girase, Principal, S.V.S's Dadasaheb Rawal College, Dondaicha for his competent moral support.

REFERENCES

[1] Shitole S. J. and Saraf K. B., (2001) "Growth and study of some gel grown group II single crystals of iodate.", *Bull. Mater. Sci*., Vol 24, pp 461-468.

[2] S. L. Garud, N. K. Mahajan, K. B. Saraf, (2009) "Study of gel grown mixed crystals of BaxCa(1–x)$(IO_3)_4$", *Bull. Mater. Sci.,* Vol. 32, No.2, pp 187-192.

[3] D. K. Sawant and D. S. Bhavsar, (2011) "SEM, PL, and UV Properties of Mixed Crystals of Ca-Ba tartrate in silica Gel", *Der Chemica Sinica,* Vol. 2, No. 3, pp 63-69.

[4] H. M. Patil1 and D. S. Bhavsar, (2011) "Crystallographic and FT-IR Characteristics of Gel Grown Cerium Tartrate Crystals*", Archives of Physics Research*, Vol. 2, No. 1, pp 239-245.

[5] S. J. Nandre, R. R. Ahire, and S. J. Shitole, (2012) "Study of Growth, EDAX, Optical properties and Surface Morphology of Zinc Tartrate Crystals", *Journal Of Nano- And Electronic Physics",* Vol. 2, No. 2, pp 04013-1 - 04013-4.

[6] Shivani Suri, K. K. Bamzai and Vishal Singh (2011) "Growth and thermal kinetics of pure and cadmium doped barium phosphate single crystal" , J. *Therm. Anal. Calorim.* Vol. 105, pp 229-238.

[7] K. D. Girase and D. S. Bhavsar, (2011) "Growth and thermal behavior of lead Iodate crystals grown in silica gel", *J. Therm. Anal. Calorim.*, Vol. 105, pp 187-190.

[8] Garud S. L & Saraf K. B. (2008) "Growth and study of mixed crystals of Ca– Cd iodate", *Bull. Mater. Sci.,* Vol. 31, No. 4, pp639-643.

[9] S. J. Joshi, B. B. Parekh, K. D. Vohra & M. J. Joshi (2006) "Growth and Characterization of Gel Grown Pure and Mixed Iron- Manganese Levo-Tartrate Crystals" *Bull. Mater. Sci.,* Vol. 29, pp 307-312.

[10] I. Quasim, A. Firdous, N. Sahni, S. K. Khosa & P. N. Kotru (2009) "Characterization of pure and doped potassium hydrogen tartrate single crystals grown in silica gel", *Cryst. Res. Technol., Vol.* 44, pp539-547.

Author

Dr. K. D. Girase
Associate Professor
Vice Principal, Dadasaheb Rawal college, Dondaicha,
Working on crystal growth and material science
Paper published = 21