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GROWTH OF SINGLE CRYSTAL OF $KClO_4$ USING VARIOUS GEL TECHNIQUES

CHAPTER - 3

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3.1 INTRODUCTION

It has been reported [1-10] that a variety of crystals suitable for research and technology can be grown in silica gel. The method is specifically useful for substances which, because of their low solubilities or low dissociation temperatures [or both as in this case] can not readily be grown in other ways. The gel medium prevents turbulence and remaining chemically inert, provides a three dimensional structure which permits the reagents to diffuse at a desirable controlled rate. Further, its softness and the uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth.

The growth of single crystals of potassium perchloride ($KClO_4$) is of considerable interest or particularly for basic studies of their electronic, optical and other pertinent characteristics.

3.2 EXPERIMENTAL DETAILS

The crystallization apparatus used in the present work consists of test tubes of 2.5 cm diameter and 20 cm length, and a beaker single tube system with a 250 ml beaker and a 2.2 cm diameter glass tube open at both ends.

The chemical reaction taking place in the gel media for the formation of crystals was,

$$KNO_3 + HClO_4 \longrightarrow KClO_4 + HNO_3$$

other types of cationic and anionic reactants have also been tried.

Silica gels were prepared by mixing pure sodium silicate (Sp.gr. 1.04) and different amounts of various acids. In order to determine the best experimental conditions leading to the growth of large and well formed single crystals, four different sets of test tube experiments were performed by adding different concentrations of feed solutions of $HClO_4$ over KNO_3 and KNO_3 over $HClO_4$ incorporated acidic gels.

In the first set, gel solutions were prepared by adding 20 ml of sodium silicate to 10 ml of 1N $HClO_4$ solution. After the gels had set, 20 ml of 1N KNO_3 solutions were added. In the second set, the gels were prepared by adding 20 ml of sodium silicate to a combination of 5 ml 2N KNO_3 + 5 ml of 2N acetic acid. The feed solutions of 1N $HClO_4$ were added on the set gels. In the third set, $NaClO_4$ or $HClO_4$ was used as one of the reactants instead of KNO_3. In the fourth set, the gels were prepared with mineral [HNO_3, HCl and H_2SO_4] and organic [acetic, propionic, citric and tartaric] acids. In this set, 1N KNO_3 and each of the above mentioned acids were added to sodium silicate to form gels. After setting of these gels, feed solutions of 1N $HClO_4$ were added. In all these four sets, the crystals have been havested after 10 to 15 days.

In a beaker-single tube system, [Fig.3.1] the gels were prepared by mixing 1N of each of the above mentioned acids [except $HClO_4$] with sodium silicate. After the gels had set, 90 ml of 1N $HClO_4$ in a tube and 70 ml of 2N KNO_3 in a beaker were added. In this case, the crystals have been havested after 2 to 3 months.

In the U-tubes [11] of different diameters varying from 2.5 to 5 cm, the neutral gels were prepared by mixing 1.04N sodium silicate and 1 to 2N acetic acid solutions. After setting the gels, the feed solution of KNO_3 and $HClO_4$ of concentrations varying from 1 to 2N were added in the two limbs of the U-tube and the crystals were allowed to grow. This method produced good single crystal 10 X 5 X 4 mm^3 size and it took eight weeks to obtain crystals of this size.

The growth apparatus used for the present study was a modification of the double-beaker system suggested by Patel and Bhat [12] and is shown in Fig.3.2. The apparatus is practically more convenient to use than the double-beaker system [12] because of its ease of handling. The two 250 ml of single-beaker were attached to a 250 ml capacity beaker by socket and cone arrangement, instead of being held vertically using external clamps, and hence there are relatively less chances of rupture of the gel during setting as well as during crystal growth in the present apparatus. This system is much more physically stable than the other gel growth systems.

In the test tube experiments the crystals grew upto 6 X 5 X 4 mm^3 in 15 days while in the beaker-single tube system they grew upto 15 X 12 X 8 mm^3 in about 70 days. The result reported here are based on the statistical average of five set of experiments.

3.3 RESULTS AND DISCUSSION

3.3.1 CRYSTAL GROWTH IN TEST TUBES

It is observed that in the case of KNO_3 as feed solution, nuclei formed only on the gel surface and not inside the gel. Moreover, the gel completely dissolved in KNO_3 solution within 12 hours. In the case of KI, after two to three days, the colour of the gel and the feed solution became reddish brown. This may be due to the formation of hydroiodic acid (HI) which might have liberated when KI reacted with perchloric acid. Regarding KF as the feed solution, the nucleation centre are more compared to those observed with other feed solution are used as feed solutions, well defined and transparent single crystal have formed.

The nucleation density is less and the size of the crystals grown is slightly bigger in KNO_3 incorporated gels, when $KClO_4$ is used as feed solution instead of $NaClO_4$. This is due to the decrease in pH of the gels in tube with $HClO_4$ as feed solution. Hydrochloric acid formed by the reaction KNO_3 with $HClO_4$, reduces the pH of gels and this increases the nucleation density. The nucleation centres occur more in $HClO_4$ incorporated gels with KNO_3 as feed solution which is due to a slighter decrease in the pH of gels by adding $HClO_4$ to sodium silicate than when KNO_3 is added. The results are shown in Fig.3.3 (a)-3.3 (b).

In $HClO_4$ set gels, the number density is less, the size is bigger and comparatively more number of crystals are transparent than in other acid set gels. In test tubes, various amounts and concentrations of $HClO_4$ to form good gel media and KNO_3 as feed solution have been tried. Out of all these, a combination of 10 ml of 1N $HClO_4$ and 20 ml of sodium silicate to form a gel and 20 ml of 1N KNO_3 as feed solution has been found to be the best in terms of crystal size, intercrystalline separation and clarity of the gel media. It is also found that the number density is less, the crystals are bigger and more perfect with increasing distance from gel-solution interface. This is due to the fact that near the gel-solution interface, the concentration gradients are higher than at lower depths of the gel. Since a few crystals are formed at greater depths from the gel-solution interface, they grow bigger in size. It has been found that the average crystal growth rate is greatest near the top of the diffusion column where the concentration gradients are high, and small near the bottom where the gradients are small. Corresponding to different growth rates, the dislocation density is also different.

3.3.2 CRYSTAL GROWTH IN BEAKER-SINGLE TUBE SYSTEM

In this method, acetic and perpionic acid set gels have been found to be the best to grow $KClO_4$ crystals. The crystals growing in acetic and propionic acid set gels

In the case of mineral acid set gels, the gels are setting either immediately or after ten days, with organic acids, gels can be set within the required time that is, the range of the gel setting period is larger in the case of organic acid set gels than mineral acid set gels, as show. However, in the case of mineral acid set gels, the pH changes rapidly compared to the organic acid set gels with an increase or decrease of a few ml of acid. The pH value of the other mineral, tartaric and propionic acid gel solutions, respectively. Also in the case of organic acids, for the same pH value, a larger amount of acid set gels are less dense and more transparent than the mineral acid set gels.

Experiments were also performed in gels setting with 1.03 sp. gr. sodium silicate and adding 1N, 2N, 3N, and 4N acetic acid or propionic acid, by keeping the pH constant at 7. It was found that lesser the concentration of acid, larger is the pH value for the same amount of acid. So pH was kept constant by adjusting the amount of 1N, 2N, 3N and 4N acids. Then, more number of transparent crystals were obtained with 1N acetic or propionic acid set gels this is due to the fact that, for the same pH value, gels with lower concentrated acids (1N) are less dense than those with higher concentrated [2 to 4] acids.

3.3.3 CRYSTAL GROWTH IN U-TUBES

In this method, using U-tubes [11] of different diameters varying from 2 to 5 cm, the neutral gels were prepared by mixing 1.04 N sodium silicate and 1 to 2N acetic acid solutions. After setting the gels, the feed solutions of KNO_3 and $HClO_4$ of concentrations varying from 1 to 2N were added in the two limits of the U-tube and the crystals were allowed to grow. This method produced good single crystals of 10 X 5 X 4 mm size and it took eight weeks to obtain crystal of this size as shown in Fig.3.4.

Most of the work on crystal growth in gels has been done by the reaction method. It has a special advantage of growing single crystal which are insoluble [or slightly soluble] in water and which decompose before reaching their melting point. The requirement to grow single crystal by this method are [i] the reactants employed here must be soluble in the solvent [usually water] and the product crystal must be relatively less soluble [ii] the gel must remain stable in the presence of the reacting solutions and must not react with these solutions or with the product formed and [iii] some solibility of the product crystal is required in order to grow crystals of any size.

In this method two soluble reactants are allowed to diffuse through a gel where they react and form an insoluble or relatively less soluble crystalline product and reactant is diffused into it or by the U-tube technique or its modifications in which the two reactants are allowed to react by diffusion into an essentially inactive gel.

3.3.4 CRYSTAL GROWTH IN MODIFIED GEL TECHNIQUE:

The experimental results reported here are an extension of earlier studies by the authors [13-15] on the crystal growth of potassium perchlorate. Conventional preparative procedure have been employed as previously described. All experiments were conducted in standard 25mm diameter test tube and the improved design used unless; otherwise specified. On trying various reactants like KNO_3

with $HClO_4$ set gels in test tubes, it was found that KNO_3 yielded the best quality crystals.

The important result to be derived from the experimental data regarding the growth condition are summarized as below :

a) The optimum growth system, yielding the highest quality and largest size $KClO_4$ crystals was based on a system utilizing the improved design (Fig.3.2) with KNO_3 and $HClO_4$ as reactive species. The growth conditions in this case are similar as except that the gels were prepared using 1N CH_3COOH and on additional amount of 120 ml gel solution added in the two side beakers, to prevent damage to the already set gel, while adding the feed solutions, the crystal product were clear and their ultimate size 20-25 mm on edge, was reached after about two to three months.

b) All growth rate cure obey the general relationship $D = K(T)^{\frac{1}{2}}$, where D = length of the crystals (cm), T = time of growth (hrs.) and K = growth rate constant (cm^2/hr), this factor is gel age dependent; its value decreases with increase in gel age. The growth rate curve of $KClO_4$ crystals in gels follow a parabolic law which is a characteristic of a one dimensional diffusion controlled process.

c) The perfection of the $KClO_4$ crystal growtn has been studied by the chemical etching technique and electron microprobe analysis. Chemical etching, using concentration of HCl and H_2SO_4 in the volume ratio 2:3 at room temperature [20 to 28°C] revealed that the average dislocation density is very low and is of the order of 10^2 cm^{-2}. These fact indicate that $KClO_4$ crystal grown, by using KNO_3 and $KClO_4$ as the reactive species.

d) The density of nucleation centres plays a vital role in the crystal size attainable, which governs the merit of the process of growth. The incorporation of small amount of concentrated HNO_3 solution helped nucleation to occur only at a few sites, which resulted in the growth of large crystals. The HNO_3 in the gel is responsible for the growth of large crystal was demonstrated by growing $KClO_4$ crystals, employing the reaction,

$$KNO_3 + HClO_4 \longrightarrow KClO_4 + HNO_3$$

1.5N aqueous solutions of both the reactants were used, which produced crystals more than 2 cm long, whereas the other reactants nevers produced large crystals.

3.4 <u>CONCLUSIONS</u>

1. for the preparation of single crystal of $KClO_4$ upto 120 mm^3 in size, suitable for IR, ESR, EPR, ionic conductivity and optical absorption spectroscopy measurements.

2. growth in test tube system has several advantages over the beaker-single tube system which requires relatively larger quantities of gels as well as feed solutions and more time. However, for crystals upto or more than 500 mm^3 the use of the beaker-single tube system is suggested.

3. In beaker-single tube experiments, acetic or propionic acid set gels with 2N KNO_3 in the beaker and 1N $HClO_4$ in the tube, as the reactants gave the best results.

4. Single crystals of potassium perchlorate upto 20 X 10 X 6 mm have been grown in silica gels acidified with acetic acid.

5. The reaction waste products have been found to considerably influence both the size and perfection.

6. In the U-tube, in the gel nearer to KNO_3 feed solution, good quality single crystal have been obtained compared to those in gel near $HClO_4$ feed solution.

7. The optimum growth system, yielding the highest quality and largest size $KClO_4$ crystals, was based on a system utilizing the improved design with KNO_3 and $HClO_4$ as the reactive species.

REFERENCES

1. H. Arend and J. Perison Mater. Res. Bull. 6 (1971) 1205.
2. David A. Glocker and I.F. Soest J. Chem Phys. 51 (199) 3145.
3. C. Konak, F. Smutny, B. Brezina and Budik Czech. J. Phys. B27 (1977) 1313.
4. S. Mennicke and W. Dittmar J. Crystal Growth 26 (1974) 197.
5. Z. Blank and W. Brenner J. Crystal Growth 11 (1971) 255.
6. S.M. Patel and Varghese George J. Elect Mater. 6 (1977) 499.
7. P.F. Kurz, Ohio.J. Science 206 (1962) 155.
8. Z. Blank and W. Brenner Nature 222 (1969) 79.
9. H.K. Henisch and C. Srinivasgopalan solid state comm. 4 (1966) 415.
10. A.E. Dugan and H.K. Henisch J.Phys. Chem. Solids 28 (1967) 971.
11. Patel, A.R. Vankateshwara Rao, A.: Bull. mater. Sci., 4 (1982) 527.
12. A.R. Patel and H.L. Bhat J. Crystal Growth 12 (1972) 288.

13. Patel A.R. and Venkateshwara Rao, A.J. Crystal Growth 38 (1977) 288.

14. Patel A.R. and Venkateshwara Rao; A.J. Crystal Growth 43 (1978) 351.

15. Patel A.R. and Venkateshwara Rao; A. Krist. Tech. 16 (1981) 1007.