Growth of larger and more perfect single crystals of KClO_4 in silica gel

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MS received 7 July 1984; revised 4 March 1985

Abstract. As part of a continuing effort on crystal growth in gels, this paper describes the growth of large transparent single crystals of KClO_4 by the improved design. The effect of various anionic and cationic components on nucleation, growth and quality of these crystals has been studied. It has been found that a combination of KNO_3 and HClO_4 as the reactants resulted in the best crystals in terms of crystal size, quality and inter-crystalline separation. The effect of various impurities on nucleation, growth and quality of these crystals has been studied. It has been found that the impurities which enhance the solubility of KClO_4 have a positive effect on the size and quality of the crystals. A new etchant, consisting of concentrated HCl and H_2SO_4 in the volume ratio 2:3 has been found to reveal as-grown as well as freshly introduced dislocations.

Keywords. Crystal growth; potassium perchlorate single crystals; growth rates; morphologies; dislocations; nucleation control.

1. Introduction

Increasing use is being made of chemical reactions in the preparation of solid-state materials. Two or more species react together to form the desired solid product along with one or more water-soluble or gaseous products. Among such reaction techniques (Nancollas and Rurdie 1963; Henisch *et al* 1965; Huber *et al* 1974; Patel and Arora 1973; Nielsen 1964; Oxley 1966), one important technique (Henisch 1973), growing single crystals in a gel, has been investigated by several laboratories (Armington and O'Connor 1971; Brezina and Havrankova 1976; Shripathi *et al* 1980). The technique is especially useful for crystals which by virtue of their low dissociation temperatures or low solubilities (or both as in this case) cannot be grown from the melt, the vapour or directly from solution. The gel medium prevents turbulence and remaining chemically inert, provides a three dimensional structure which permits the reagents to diffuse at the desired controllable rate. Further, its softness and the uniform nature of the constraining forces that are exerted upon the growing crystals encourage orderly growth.

In the preliminary studies on the growth of KClO_4 single crystals, Patel and Venkateswara Rao (1977, 1978, 1981) have reported the successful growth of these crystals and the effect of different gel parameters on nucleation and growth along with the microstructures of these crystals in gels. The present paper reports, the results of the detailed studies which yielded more perfect and larger single crystals of potassium perchlorate by using the improved design (Patel and Venkateswara Rao 1980) as the

Table 1. Experimental data on the growth of KClO_4 single crystals using various crystallization apparatus and different acid-set silica gels with KNO_3 and HClO_4 as the reactants.

Crystallization apparatus	Acid solution in gel	Additional reagent in gel	Feed solutions	Maximum crystal size (mm^3)	Growth period (days)	Observations
Test tubes	H_2SO_4	0.1 to 2 N KNO_3	0.1 to 2 N HClO_4	$4 \times 3 \times 2$	15	Liesegang rings formed. Single crystals formed in between the Liesegang rings.
Test tubes	HCl	0.1 to 2 N KNO_3	0.1 to 2 N HClO_4	$4 \times 4 \times 3$	15	Nucleation density is greater as compared to HNO_3 and HClO_4 acid set gels.
Test tubes	HClO_4	—	0.1 to 2 N KNO_3	$7 \times 6 \times 5$	15	Nucleation density lesser than in HCl set gels but greater than in HNO_3 acid set gels.
Test tubes	HNO_3	0.1 to 2 N KNO_3	0.1 to 2 N HClO_4	$8 \times 6 \times 5$	15	Nucleation density lesser than in HClO_4 acid set gels.
250 ml beakers	HNO_3	0.1 to 2 N KNO_3	0.1 to 2 N HClO_4	$6 \times 5 \times 3$	15	Nucleation density is greater as compared to the nucleation density in test tubes under the same conditions.
U-tubes	HNO_3	—	(a) 0.1 to 2 N HNO_3 (b) 0.1 to 2 N HClO_4	$9 \times 7 \times 4$	25	At higher concentrations ($> 1.5 \text{ N}$) of both the feed solutions the number of needles are greater, whereas platelets are larger in number at low (0.2 to 1 N) concentrations.
Beaker-single tube system	HNO_3	—	(a) 0.1 to 2 N HNO_3 (b) 0.1 to 2 N HClO_4	$15 \times 9 \times 7$	30	Only a few nucleation centres formed using feed solutions of 0.1 to 0.5 N in the tube and 0.8 to 1.5 N in the beaker.
Modified-gel system	HNO_3	—	(a) 0.1 to 2 N HNO_3 (b) 0.1 to 2 N HClO_4	$10 \times 12 \times 8$	90	Growth period was greater (3 months) due to small amounts of feed solutions in the side tubes.
Improved design (figure 1)	HNO_3	—	(a) 0.1 to 2 N HNO_3 (b) 0.1 to 2 N HClO_4	$25 \times 15 \times 12$	65	Best crystals, in terms of size and quality, were obtained with 1.5 to 2 N of both the feed solutions (figure 2)

growth apparatus and by using KNO_3 and HClO_4 solutions as the reactants along with some impurities.

2. Experimental, observations and discussion

The experimental results reported here are an extension of earlier studies by the authors (Patel and Venkateswara Rao 1977, 1978, 1981) on the crystal growth of potassium perchlorate. Conventional preparative procedures have been employed as previously described. All experiments were conducted in standard 25 mm dia test tubes and the improved design used unless otherwise specified. On trying various reactants like KOH , KF , KI , KCl , KBr and KNO_3 with HClO_4 set gels in test tubes, it was found that KNO_3 yielded the best quality crystals, the optimum growth conditions for which are given in table 2. Some of the other experimental details and observations are summarized in table 1.

The important results to be derived from the experimental data regarding the growth conditions are summarized 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 (figure 1) with KNO_3 and HClO_4 as the reactive species. The growth conditions in this case are similar as in table 2 except that the gels were prepared using 1 N HNO_3 and an 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 products were clear and their ultimate size, 20–25 mm on edge, was reached after about two to three months (figure 2).
- (b) The growth rates of crystals in a typical growth system are described in figure 3. All

Figure 1. Schematic diagram of the improved design to grow KClO_4 crystals.

Table 2. Optimum growth conditions to obtain the best quality single crystals of KClO_4 using test tubes.

Specific gravity of sodium silicate (20 ml)	: 1.03
Acid added to form gel solution (10 ml)	: 1 N HClO_4
pH of the initial gel solution	: 2.5 to 4
Feed solution over the gel (30 ml)	: 1 N KNO_3
Crystallization temperature	: 24 to 28°C
Gel setting time	: 20 hrs

Figure 2. A few single crystals of KClO_4 grown by the improved design (5 mm grid). **Figure 3.** Growth kinetics of crystalline KClO_4 needles in a gel 125 hrs (curve I) and 218 hrs old (curve II).

growth rate curves obey the general relationship $D = K(T)^{1/2}$, 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 decreased with increasing gel age. The growth rate curves of KClO_4 crystals in gels follow a parabolic law which is a characteristic of a one-dimensional diffusion controlled process.

(c) The morphologies of various crystals, grown under different conditions with KNO_3 and KClO_4 as the reactants in test tubes, have been examined optically. Crystals belonging to five different morphologies have been identified, as shown in figures 4(a)–(e). Figure 5 shows the corresponding schematic diagram of the morphologies.

(d) The perfection of the KClO_4 crystals grown has been studied by the chemical etching technique and electron microprobe analysis. Chemical etching, using con-

Figure 4. Different habits of KClO_4 single crystals grown under different conditions (size: 7 mm across), (a) at very low concentrations (0.5 to 1 N) of both the reactants, (b) at medium concentrations (0.5 to 1 N) of both the reactants, (c) at very high concentrations (2 N) of both the reactants, (d) at one of the reactants at higher (2 N) and the other at lower (0.1 to 0.4 N) concentrations, (e) at higher temperatures ($> 35^\circ\text{C}$) and at higher concentrations (2 N) of both the reactants.

centrated HCl and H_2SO_4 in the volume ratio 2:3 at room temperature (20 to 28°C) revealed that the average dislocation density (figure 6) is very low and is of the order of 10^2 cm^{-2} . Some small crystals (upto $6 \times 5 \times 4 \text{ mm}^3$) are free of dislocations. Electron microprobe analysis of the crystals indicated that there are no detectable impurities upto a few ppm. These facts indicate that the KClO_4 crystals grown, by using KNO_3 and HClO_4 as the reactive species, are highly perfect. Figure 7 shows that the above etchant is capable of revealing freshly introduced dislocations also.

Figure 5. Schematic diagram of the habits shown in figure 4 (a)–(e).

Figure 6. Etch pattern on $\{001\}$ face of KClO_4 crystal with etching time 8 min $\times$ 150.

Figure 7. Etch pattern of freshly introduced dislocations on $\{001\}$ face of KClO_4 crystal $\times 125$.

(e) Nucleation control: In attempts to grow still larger and more perfect crystals, small amounts of several reagents such as concentrated HCl , HBr , HI , H_2SO_4 , HF , HNO_3 and CH_3COOH were incorporated into the gel itself before setting, and it was observed that the addition of HNO_3 produced encouraging results. With the addition of 15 ml of concentrated HNO_3 solution to 300 ml of pre-set gel, with the improved design, only a limited number of nucleation sites developed which resulted in the growth of prismatic crystals upto $2.5 \times 1.5 \times 1.2 \text{ cm}^3$. A few of the KClO_4 crystals grown by this method are shown in figure 2.

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 a small amount of concentrated HNO_3 solution helped nucleation to occur only at a few sites, which resulted in the growth of large crystals. This is due to the increased solubility of KClO_4 in water containing HNO_3 solution (figure 8). That the HNO_3 in the gel is responsible for the growth of large crystals was demonstrated by growing KClO_4 crystals, employing the reaction

1.5 N aqueous solutions of both the reactants were used, which produced crystals more than 2 cm long, whereas the other reactants never produced crystals as large.

3. Conclusion

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.

Figure 8. Solubility of KClO_4 versus different temperature for normalities of HNO_3 solution.

Acknowledgements

The author is thankful to Prof. R N Patil for his kind encouragement. He is also thankful to Mrs A Parvathi Rao for help during the preparation of the manuscript. The present work is supported in part by a project grant from the ugc, New Delhi.

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