Nucleation and growth of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ single crystals in silica gels

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Abstract. As part of our work on growth of cadmium oxalate single crystals in gels, we describe here variation of nucleation density and growth of these crystals as a function of concentration of feed solution, gel ageing, gel density, gel pH and intermediate neutral gel column. While high density and high pH gels have been found to produce opaque crystals, good quality transparent single crystals have been obtained in low density and low pH gels. It was observed that the intermediate neutral gel column and gel ageing considerably reduced the number of nucleation sites and increased the size of the crystals without affecting their quality. By concentration programming the size of the crystals increased.

Keywords. Gel growth; crystal growth; silica gel; cadmium oxalate crystals; nucleation control.

1. Introduction

The problem of nucleation in crystal growth is of great importance in practical applications, since the crystals which grow in any particular gel system compete with one another for solute. This competition limits their size and perfection, and it is obviously desirable to suppress nucleation until, ideally, only one crystal grows in a predetermined location. The available techniques have not yet reached this level of perfection.

In gel growth, nucleation control can be achieved to some extent by changing a variety of gel parameters, viz. concentration of feed solutions, gel density, gel pH, intermediate neutral gel column and concentration programming. Transparent single crystals of cadmium oxalate have been obtained between pH values 4.5 and 6.5 (Bandyopadhyay and Ashok 1977). Blank *et al* (1968) and Randive *et al* (1969) show that nucleation can be controlled using intermediate neutral gels. Nucleation control by concentration programming has been described for various crystals (Henisch *et al* 1970). Influence of gel ageing and gel density on various crystals has been studied by several workers (Brezina and Havrankova 1971; Halbestadt *et al* 1969). The successful growth of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ crystals using various crystallization apparatuses has been described in our previous paper (Shedam and Rao 1993). This paper deals with the effects of gel parameters on nucleation and growth of CdC_2O_4 crystals.

2. Experimental procedures

Crystal growth experiments were carried out in one-end-open Corning glass tubes of length 20 cm and inner diameter 2.5 cm. The chemicals used were Loba G.R. CdCl_2 and B.D.H. 'AnalaR' perchloric and oxalic acids.

The following chemical reaction was employed for the growth:

The gel solutions were prepared by mixing a pure solution of sodium silicate with required amount of 1 N or 0.5 N oxalic acid. The gel solutions thus prepared were then transferred to test tubes and allowed to set at room temperature. After the gels were set, feed solution of CdCl_2 was placed above the gels for crystallization. Double distilled water was used throughout. Completion of crystallization (with crystal size up to $5 \text{ mm} \times 3 \text{ mm} \times 2 \text{ mm}$) took about 20 days. The results are based on the average of five sets of experiments.

3. Observations and discussion

3.1 Effect of gel density

Gels of different densities were obtained by mixing sodium silicate of specific density from 1.01 to 1.06 g/cm^3 with 1 N oxalic acid, keeping the pH constant at 5 by adding a few drops of perchloric acid. It was observed that the transparency of the gel decreased as the gel density increased. Also, the gels with higher densities set faster than the gels with lower densities. It may be noted that well-defined and transparent single crystals were obtained with sodium silicate of specific density 1.03 g/cm^3 , as shown in figure 1. On the other hand, gels of specific density below 1.03 g/cm^3 took a long time (more than a month) to set and were mechanically not very strong. A specific density of 1.02 g/cm^3 was found to be the lowest practical limit. It is clear from figure 2 that an increase of gel density decreases the nucleation density. This is because greater gel density results in smaller pore size, which is in agreement with the observations made by Henisch (1970).

3.2 Effect of pH of gels

The pH value of gels was varied from 2 to 10 by adding a few drops of perchloric acid before setting of the oxalic acid gel solutions. It was observed that as the pH increased the transparency of the gel decreased. The crystals growing at higher pH values were not transparent and well defined. This was due to contamination of the

Figure 1. A few transparent and well-defined crystals of cadmium oxalate grown in gel of density 1.03 g/cm^3 .

Figure 2. Number of crystals vs density of Na_2SiO_3 (g/cm^3) gel.

Figure 3. Number of crystals vs pH of the gel.

crystals with silica gel, because as the pH increased the box-like network structure of the gel changed to a loosely bound platelet structure which lacked cross-linkages; the cellular became less distinct (Henisch 1970). It was found that as the pH of the gel increased the number of crystals decreased, and at very high pH (> 9) the crystals were not well defined. Figure 3 shows that the total number of crystals decreased with increase in the pH, which may be due to improper formation of cells at high pH gels.

3.3 *Effect of concentration of feed solution*

To study the effect of concentration of feed solution, gels of same pH and density were prepared. Feed solutions of different concentrations varying from 0.5 to 1.5 N were added over the set gels. Figure 4 shows crystals growing in gels at three different concentrations of feed solutions. It is clear from the figure that as the concentration increases the number of crystals increases. This indicates that at higher concentrations of feed solutions, because of enhanced availability of cadmium ions, the nucleation density increases.

3.4 *Effect of ageing of gels*

To investigate the effect of gel ageing, gels were allowed to age for various periods before adding the feed solution. Crystals growing in gels allowed to age for three different periods are shown in figure 5. It is clear from the figure that as the ageing of the gel increases the number of crystals decreases. As reported by Henisch (1970) gel ageing reduces the cell size and consequently the rate of diffusion of ions into the gel. Gel ageing has no pronounced effect on the size or the quality of the crystals.

3.5 *Effect of intermediate neutral gel*

To study the effect of the height of the intermediate neutral gel column, different amounts of perchloric acid set gel solutions were added over the oxalic acid set gels.

Figure 4. Crystals growing at three different normalities of CdCl_2 solution: (a) 0.5 N, (b) 1.0 N, (c) 1.5 N.

Figure 5. Crystals growing in gels aged for: (a) 5 days, (b) 15 days, (c) 25 days.

Figure 6. Crystals growing in tubes with three different heights (L) of intermediate neutral gel columns: (a) $L = 0$ cm, (b) $L = 4$ cm, (c) $L = 6$ cm.

The neutral gels were also allowed to set and the feed solution was then added. Figure 6 shows the crystals growing in tubes with different heights of intermediate neutral gel columns.

The intermediate neutral gel slows down the reaction between the reactants, reducing the number of critical nuclei. The intermediate neutral gel increases the size of the crystals considerably without affecting their quality.

3.6 Nucleation control by concentration programming

Over the oxalic acid set gel, 30 ml of 0.2 N CdCl_2 solution was placed. The strength of this feed solution was increased at the rate of 0.01 per day by removing 20 ml of the above feed solution and replacing it with an equal amount of higher concentration feed solutions. The process was continued till the concentration of CdCl_2 reached around 2.5 N, when nucleation started and resulted in a few nucleation centres. Figure 7a, b shows crystals growing without and with concentration programming, respectively. It is considered that with very dilute reactant, the amount of material diffused through the gel is small and hence the rate at which supersaturation is attained is low. Under these circumstances, a few nuclei are formed. On increasing the concentration, further growth of existing nuclei is preferred to the formation of additional ones. Crystals grown by this method are transparent and larger than those grown without this method.

Figure 7. (a) Crystals growing without concentration programming and (b) crystals growing with concentration programming.

4. Conclusions

Transparent single crystals of $\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ can be obtained at low pH values (below 6) with low density of gels (below 1.04 g/cm^3) of sodium silicate. Gel ageing and intermediate neutral gel column reduce nucleation density while increase in concentration of the feed solution increases it. By concentration programming, the size of the crystal can be increased.

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