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Synthesis and Size Optimization of Crystals Grown by the Mixed Gel-Solution Technique

Two experimental devices have been used with the aim to optimize the synthesis of single crystals by means of the mixed gel-solution technique. These consist of a gel source-reservoir saturated at T_0 and a vessel of aqueous solution saturated at T_f. $T_0 > T_f$. In such devices, the evolution of the supersaturation in the vessel of aqueous solutions allows that the growth process to be controlled by such a source-reservoir and the crystal itself. Average growth rates of 3 and 4 mm/day have been found for KDP crystals.

Dos dispositivos han sido usados para la obtención de monocristales mediante la técnica mixta de gel-solución. Estos constan de una fuente-depósito de gel saturado a T_0 y un recipiente de solución acuosa saturado a T_f. $T_0 > T_f$. La evolución de la sobresaturación en el recipiente de solución acuosa ha permitido que el proceso de crecimiento sea controlado por la fuente-depósito de gel y el propio cristal. Se han medido velocidades medias de crecimiento para cristales de KDP de 3 y 4 mm/dia.

1. Introduction

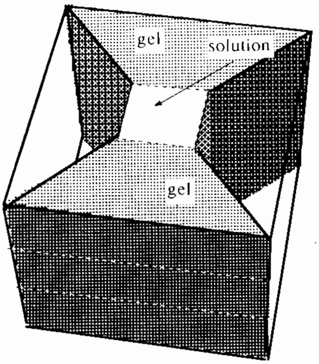
The use of the crystal growth technique in gels to obtain single crystals suitable for industrial applications is still a project for the future (GARCÍA-RUIZ). The main disadvantages disregarding such an application are a) the low average crystal growth rates (CHERNOV) and b) the small of the crystals. On the contrary, this technique presents a number of advantages, for instance, the high quality of the crystals grown in gels, including even free-dislocations crystals (BREZINA, HORVATH), and the low cost of the technique.

The aim of this work lies in determining whether the growth rate, the size of the crystals and the efficiency of the technique are variables the upper limits of which have been reached or whether, on the other hand, it is worthwhile to work on new designs oriented to enhance the current performances. The present study is confined to the case of soluble substances using a mixed gel-solution technique.

2. Experimental Method

A preliminar design has already been described in a previous work (SANTOS, CARCÍA-RUIZ). The design is supported on the fact that the induction time in gelled media is longer than in a free solution. Thus, once a seed is introduced in a saturated solution in contact with a gelled source, it works as a sink of concentration, and as a result mass flow from the gelled solution to the aqueous solution is exhausted by the growth of the seed.

The growth cell consists of two kinds of devices: A) the first recipient consists of two gel source reservoirs with a truncated pyramidal shape. Both reservoirs are separated by a rectangular shaped vessel (90 mm × 38 mm), that contains the aqueous solution into which the seeds is introduced (Fig. 1). The relation gel volume/solution volume is 400 cm^3/120 cm^3 for this device. To avoid mechanical instability of the gel volume, each source-reservoir was divided into three communicating compartments. B) This device is almost cubic in shape and consits of a rectangular source-reservoir with a section of a)



b)

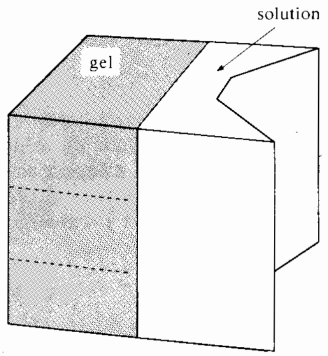


Fig. 1. Lay-out of the growth cell. a) the first device, b) the second device

100 mm × 86 mm, divided into three interior communicating compartment. The rest of the vessel is used for the storage of the aqueous solution (Fig. 1). The relation gel volume/solution volume is $320\ cm^3/320\ cm^3$.

The source reservoirs were filled with a gellified KDP solution saturated at 40 °C and pH 5. The sol was prepared by mixing the KDP solution with tetrametoxysilane (TMOS) at 5% in volume. The sol of KDP is poured when one of the source-reservoir is in horizontal position and kept at a higher temperature for 24 hours to facilitate gelling and the elimination of possible nuclei. The same operation is also performed on the other truncated pyramidal part of the first device. After 48 hours the device is than slowly cooled down to avoid abrupt contraction of the gel and is introduced into a bath of a constant temperature of 25 °C. The aqueous KDP solution is then poured to permit full contact between the gel and the solution. The seed is introduced and the growth process starts.

Once the seed is introduced, the evolution of supersaturation in the aqueous solution is unknown and as has been mentioned, two different gel sections and different relation gel volume/aqueous solution volume act as supersaturation regulating mechanisms.

2.1. Description of the evolutive process of the concentration

The evolution of the supersaturation inside the aqueous solution was obtained by conductimetry. Previously, the conductivity/concentration curve was obtained from undersaturated solution at 25 °C adding small amounts of KDP until the saturation concentration was reached (see Fig. 2). The values of saturation concentration and conductivity values for that temperature are $24.09\ g/100\ cm^3$ and 80 mS/cm respectively.

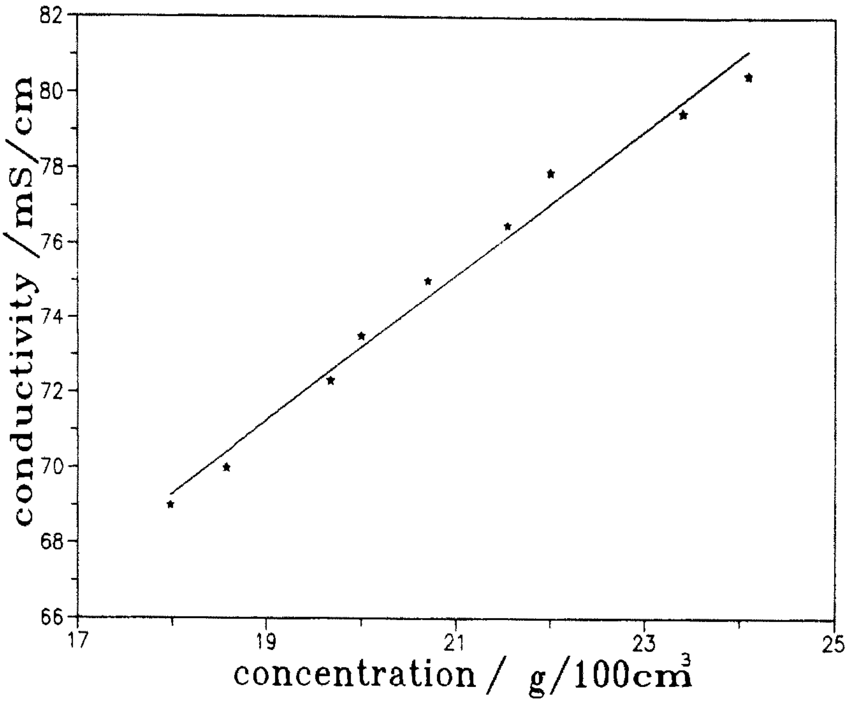


Fig. 2. Relation conductivity/concentration. The aqueous solution is maintained at constant temperature (25 °C)

To achieve the abovementioned purpose, several gellified KDP solutions saturated at 40 °C and 30 °C at 5% TMOS in volume a pH 5 were prepared. These temperature values correspond to higher concentrations (28.6 g/100 cm^3) and to the saturation concentration range (24.1 g/100 cm^3) of the aqueous solution satured at 25 °C, respectively. It's known the modification on the initial eqilibrium concentration of KDP in solutions on the mixing with TMOS (Santos, García-Ruiz).

As for the aqueous solution contained in the vessel various concentrations values have been used and are shown by their equivalent in mS/cm. For the gellified solution at 40 °C an aqueous solution concentration of 77.6 mS/cm was used whereas for the gellified solution at 30 °C, 57, 74.5 and 80 mS/cm were used respectively. All these values except for the last one correspond to undersaturated solutions at 25 °C.

In these experiments the conductivity cell was introduced in the vessel of the aqueous solution, which was continously maintained under stirring conditions.

2.2. Results

In Figure 3 are show curves, A, B, C (gellified KDP solution at 30 °C) and D (gellified KDP solution at 40 °C) that correspond to the conductivity evolution of the aqueous solution. Curves A and B (57 and 74.5 mS/cm) maintain a parabolic behaviour. In curve C (80 mS/cm), the conductivity value is constant in time. In both media, gel and solution, this value is the equivalent at saturation concentration. In curve D (77.6 mS/cm) the parabolic tendency is confirmed but when it is within the saturation concentration range the seed is

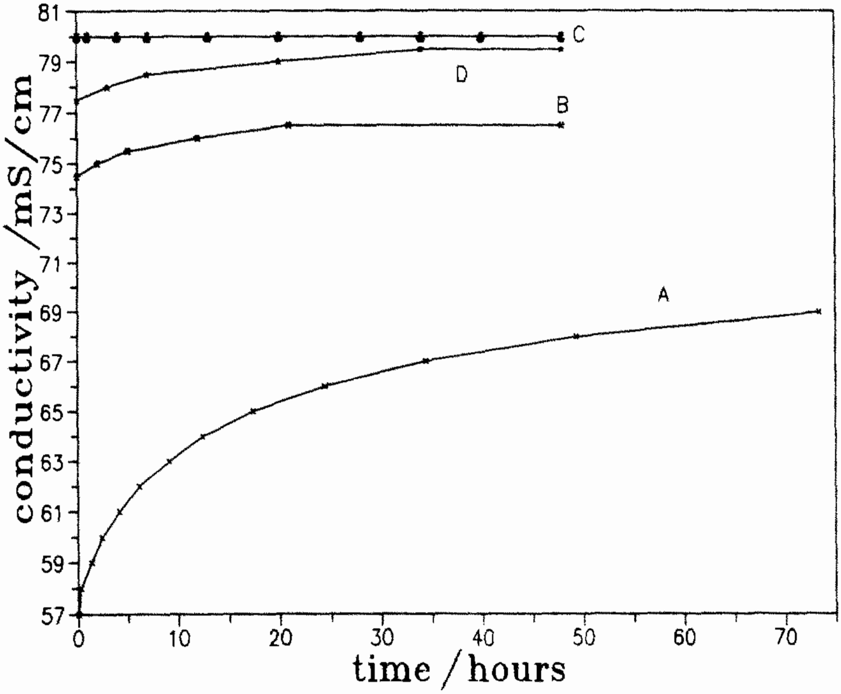


Fig. 3. Variation of the conductivity versus time at constant temperature (25 °C)

introduced and conductivity is maintained constant in time, which indicates that the flux of ions towards the reservoir of the solution is exhausted by the growth of the seed.

In accordance with the conditions described for curve D various experiments using the device shwon in Figure 1 have been carried out. For the first device, the average growth rates are 3 and 4 mm/day. These values are comparable with those obtained by other industrial crystallization methods (LOIACONO et al.; YOKOTANI et al.; VEINTEMILLAS-VERDAGUER et al.). In all experiments, however there appears a precipitate on the bottom of the rectangular vessel at the end of the process.

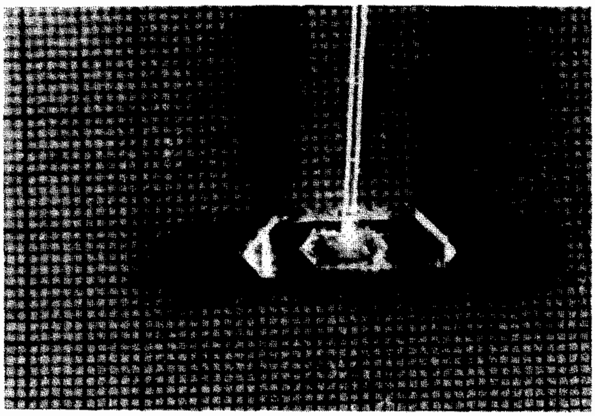


Fig. 4. A crystal obtained with the second device

For the second device, the ions flux from the gel to the solution has a behaviour identical to the one shown in curve D of Figure 3 and reaches the saturation concentration after 24 hours. Once the growth process is finished no precipitation is observed on the bottom of the vessel containing the aqueous solution and the quantity of crystals in the interior of the gel (3.2 g) is extracted which, in its turn, is followed by the weighing of the three seeds 8.2 g (8 g the crystal and 0.2 the germen), one of them is shown in Figure 4. The result obtained shows an efficiency of around 70%. The value of the average growth rate of the crystals, is similar to the rate obtained by the previous device.

3. Discussion

The concentration evolution inside the vessel of the aqueous solution can be deduced from figures 2 and 3. According to the first there is a linear relationship between the conductivity and concentration, which implies that behaviour of the latter variable, Figure 5, is identical to the behaviour of the conductivity for both devices. In the second device, the seed is introduced when the concentration saturation is reached (24 h) and the conductivity remains constant in time. Hence, the regulating mechanisms are controlled by the gel source-reservoir and the crystal itself.

Once the experiments have been finished a simple mass balance is made: $(C_0 - C_f)$ $Vg/100 = \Delta m$. Where, C_0 = grams of KDP in the gellified solution at T_0 (40 °C); C_f = grams of KDP in the aqueous solution at T_f (25 °C); V_g = gel volume. In the first device the total mass of KDP contained in the gel is 18.04 g, whereas the crystal that appeared in the

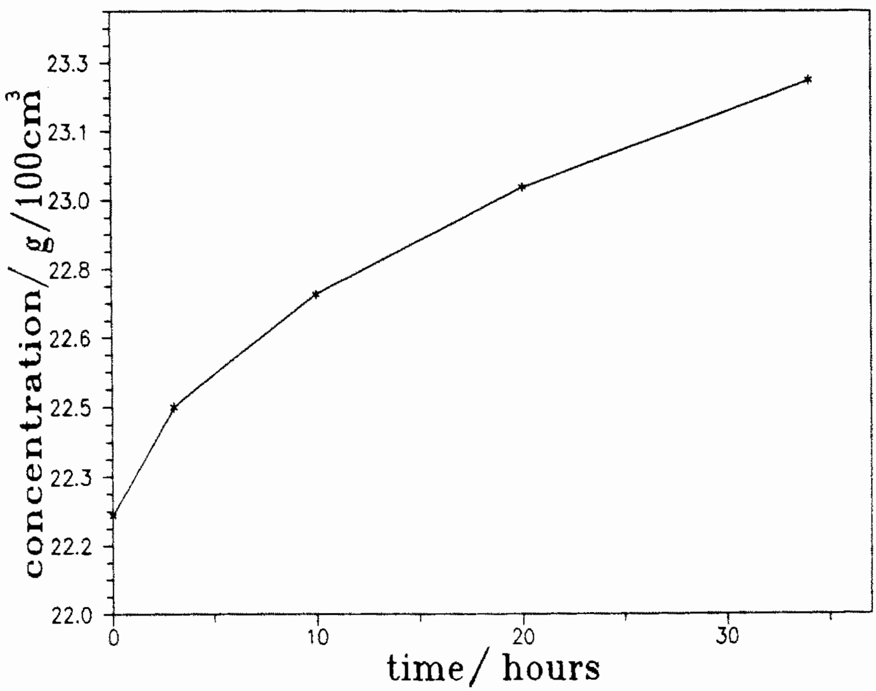


Fig. 5. Variation of the concentration versus time. These values are obtained of curve D (Fig. 3)

recipient weigh 11 g (5.540 g in the gel, 5.560 g in the solution). Nevertheless, as an undersaturated solution was used approximately 1 g (the equivalent up to reaching the concentration saturation) has to be subtrated of initial mass of KDP in the gel. These results indicate that the growth process is not yet exhausted. However, for the second device the mass contained in the gel is 14.4 g and once the quantity up to reaching saturation has been subtracted, 3.2 g, it follows that the growth had already fininshed before the experiment was interrupted as the crystals contained in the gel and the seed weigh 11.4 g.

Because of the experimental conditions and results described above, it would be interesting to know the maximum size that can be obtained with this design as well as, the duration of the experiment with a given growth velocity.

To solve these two questions the morphology of the KDP projected on (100), should be considered (Fig. 6).

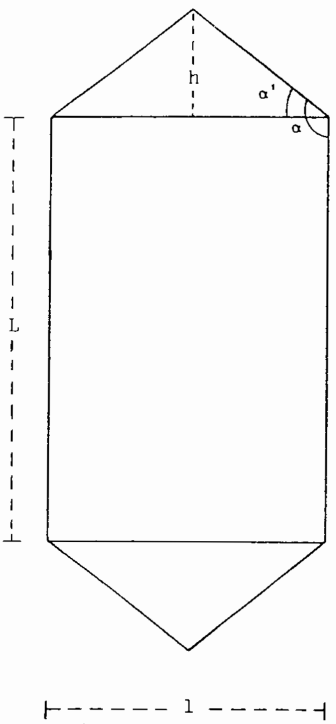


Fig. 6. The equilibrium morphology of KDP projected on (100)

The volume of this crystal is the summation of the volume enclosed by the prism plus the volume enclosed by the pyramidal faces.

$$V_{cr} = l^2 L + 2(1/3)\, l^2 h \tag{1}$$

where l, L and h are represented in the figure. This can also be expressed as

$$V_{cr} = l^2(L + 2(1/3)\, l^2 (l/2) \tan \alpha') \tag{2}$$

since, $h = l/2 \tan \alpha'$, considering $\alpha' = \alpha - 90$, being $\alpha = 133°$. Finally we have

$$V_{cr} = l^2(L + (1/3)\, l \tan \alpha') \qquad (3)$$

for the case of these experiments, the relation $L/l = 2.5$, and expression (3) becomes

$$V = 2.8 l^3 \qquad (4)$$

which for a seed of $L = 5$ mm and $l = 2$ mm the volume of the seed is 22.18 mm^3. The length of direction [001] will be $D_{001} = 6.81$ mm.

For the effectiveness to be 100% the quantity of mass that the crystal should grow is 14.43 g. Given the density of the KDP = 2.33 g/cm^3, the grown volume is 6190 mm^3 and the total volume is 6212.18 mm^3. From (4) we can know the new values of l, L, h and D_{001}, which are 13.02 mm, 32.55 mm, 12.13 mm, and 56.81 mm, respectively. Taking into account that the average growth velocity is 3 mm/day, a growth time of approximately 9 days is obtained.

Conclusions

Finally, the results of the present work demonstrate that the growth rate values are comparable to those obtained by other industrial crystallization techniques. Likewise, the efficiency obtained and the low cost of producing a crystal without the need to use highly sophisticated techniques and equipment.

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