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Original Papers

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Growth of KDP Single Crystals by Temperature Reduction under Diffusion Transport

Growth rates of 37 μm/hour for {010} faces and 40 μm/hour for [001] directions have been found for KDP crystals growing in gelled media by temperature reduction. These values, higher than those recorded in alcohol-diffusing techniques are in the range of more classical methods. A device for obtaining larger crystal size is also described.

Se han crecido cristales de KDP en geles de TMS por descenso de temperatura, con velocidades de crecimiento de 37 μm/hora para las caras {010} y 40 μm/hora para la direccion [001]. Estas velocidades, estan en el rango de los metodos clásicos, y son mayores que las registradas por las técnicas de difusion de alcohol. Se describe tambien, un nuevo diseño para la optimizacion del tamaño de los monocristales.

1. Introduction

Gel growth of crystals of soluble substances such as KDP, present a lower concentration of defects than those obtained by classical solution methods (LEFAUCHEUX et al.). Recent studies (GARCIA-RUIZ et al.) show that the growth rates of KDP single crystals prepared by this technique from hydroalcoholic solutions previously gelled, are in the range of the rates measured in industrial crystallization. Therefore, for the future application in this field of the gel technique (a more appropriate term is diffusing-reaction systems, hereinafter, D-R) a last barrier must be overcome: the optimization of the crystal size to the adequate technological range. The use of the alcohol diffusing variant, even with the three-layer method presents problems regarding the control of supersaturation and nucleation density, when larger crystals are required. Thus, it seems that the use of the temperature reduction variant is more apt for obtaining crystals of an appropriate size.

In this paper, we will discuss the data obtained on the nucleation and crystal growth behaviour of KDP crystals growing in gelled media by temperature reduction. Taking advantage of this study, the authors also propose a new design which is mainly based on the delay of induction time in gelled media in relation to free solution. Preliminary results obtained in a prototype device are described and the technical problems found are discussed.

2. Experimental

To study the nucleation and growth kinetics of the KDP crystals we have used a growth cell made up by two parallel glass plates, separated by PVC spacers. These spacers have

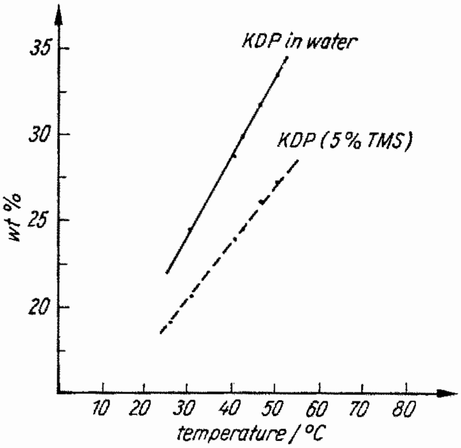

Fig. 1. Solubility versus temperature for (a) KDP solutions at pH 5, and (b) for KDP gelled solutions with TMS (5 %) at pH 5

two small holes with needles, one used for the injection of the sol and the other as air output. The perimeter of the cell is sealed with silicone. The inner cell dimensions are 75 × 103 × 4.5 mm, and its volume 35 cm^3.

KDP water solutions were saturated at temperature T_0 and its pH adjusted to 5 with NaOH. The sol was prepared by mixing these KDP solutions with tetramethoxysilane (TMS) at 5% in volume under continuous stirring. Once the sol was gelled, the apparatus was cooled in air to room temperature $T_f = 26 \pm 1$ °C. Temperature decreament was monitored by using a thermocouple inserted in the growth cell. The time elapsed t_e up to the observation of KDP precipitation under binocular lens (× 25) was also registered. In order to compare t_e for both, aqueous and gelled KDP solutions the same study was carried out with growth cells filled with water solutions of KDP of pH 5 saturated a T_0.

In order to understand the behaviour of KDP crystals growing in TMS gels, it is necessary to consider the polycondensation of this substance (AREND, CONNELLY):

$$2\,(CH_3O)_4Si + H_2O \rightarrow (CH_3O)_3Si{-}O{-}Si(CH_3O)_3 + 2\,CH_3OH\,. \tag{1}$$

The formation of methanol derived from (1) produces a noticeable modification on the initial equilibrium concentration of the KDP solutions. In fact, once the sol was prepared under the experimental conditions above described, a precipitate was produced which after filtering was identified by X-Ray diffraction (power method) as KDP and NaOH. The NaOH crystals were dissolved with ethanol and the remaining KDP solid after filtration was weighed in order to obtain the solubility of the KDP in TMS gels at 5% in volume and pH 5. The solubility of KDP in water at pH 5 was also investigated in a similar way. Figure 1 shows these data of solubility versus temperature. The solubility reduction of KDP in gels of TMS is obviously an effect of the formation of methanol during polycondensation. Therefore, for growth kinetic studies, it is important either to filter the sol before its injection into the growth cell or to use reduced solubility curve shown in Fig. 1.

3. Nucleation and growth behaviour

Two growth cells, one containing the gelled KDP solution saturated at T_0 as above described and the other containing a saturated solution of KDP at the same temperature were placed in a room kept at 26 ± 1 °C. Four T_0 values (50, 46, 42, and 40) were investigated. The temperature (T) decreases following the Cooling Newton's Law:

$$Ln\big((T - T_f)/(T_0 - T_f)\big) = -K_0 t + C \tag{2}$$

Table 1

Cooling (t_c) and nucleation times in gelled $t_e(g)$ and water solutions $t_e(s)$ of KDP

T_0	t_c	$t_e(s)$	$t_e(g)$
50	42′	280′	24 hours
46	41′	360′	28 hours
42	33′	480′	> 7 days
40	25′	720′	> 7 days

where t stands for time (seconds) and with $T_f = 26 \pm 1$ °C. Table 1 shows the values of t_c (i.e., the time at which $T = T_f$) and t_e for different T_0 investigated. For instance, for $T_0 = 50$ °C, the temperature of the growth cell becomes 26 °C, for $t_c = 42$ minutes and 240 minutes later, some crystals become visible under binocular lens (× 25) in the growth cell containing the aqueous solution, while in the growth cell containing the gel, the "nucleation time" t_c, increases to 24 hours. Similar behaviour was observed for other T_0 values concluding that there is a delay in the nucleation time as an effect of the gelling. From data displayed in Table 1 and Figure 1, it is also important to note that for the range of T_0 investigated, nucleation occurs some hours after the final temperature was obtained and therefore at high supersaturation values.

Once nucleation took place, the growth cell containing the gelled media was placed under an optical microscope kept at room temperature and growth rates were measured by time lapse microphotography. Magnification in the film was × 13 or × 33, and the period of the sequence regulated by time controller operating the microphotographic device was 15 or 5 minutes. The growth rate R_{100} of (100) faces and the growth rate R_{001} along the [001] direction (Z axis) were obtained by measuring on the film the width L_{100} and the height L_{001} of the crystal on a (010) projection. The distances L_{001} and L_{100} were obtained from the film using a astrophotometric measurer Ascorecord (Zeiss). Growth rates are given by:

$$R_{001} = \frac{dL_{001}/2}{dt} \quad \text{and} \quad R_{100} = \frac{dL_{100}/2}{dt} . \tag{3}$$

Typical average growth rates for a range of 8 hours are:

$$R_{001} = 45\ \mu\text{m/hour} \quad \text{and} \quad R_{100} = 37\ \mu\text{m/hour} \quad \text{for} \quad T_0 = 40\ ^\circ\text{C},$$

and

$$R_{001} = 40\ \mu\text{m/hour} \quad \text{for} \quad T_0 = 46\ ^\circ\text{C}$$

which are even higher than those found in the alcohol-diffusing method (GARCIA-RUIZ et al.). For $T_0 = 46$ °C the maximum growth rate measured was $R_{001} = 51$ µm/hour.

A typical plot of L_{001}^2 versus time is shown in Figure 2 for $T_0 = 40$ °C. As expected, there is a linear relationship between L^2 and t which suggest that volume diffusion is the step controlling the crystal growth process.

It is important to note that the deviation from linearity observed in Figure 2 has, been carefully checked by the authors. If bulk diffusion is the step controlling growth and assuming an inexhaustible source of material then:

$$\frac{dL^2}{dt} = \text{Constant} . \tag{4}$$

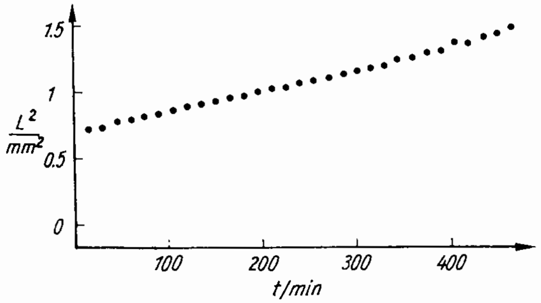

Fig. 2. Plot of L^2 versus t for [001] direction of a KDP single crystal

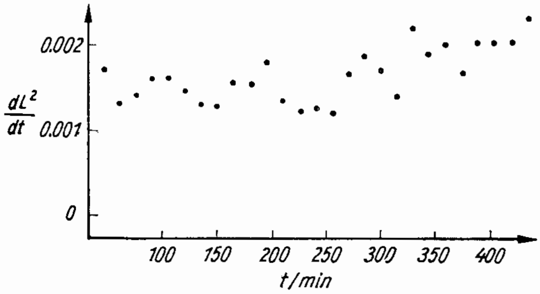

Fig. 3. Oscillatory behaviour of the growth rate in diffusing-reacting systems

However, as seen in Figure 3, the data show a clear oscillation around the constant k, which could be explained as the equivalent for single crystals of the dissipative structures such as Liesegang rings obtained for polycrystalline precipitation in diffusion-reaction systems (HENISCH, GARCIA-RUIZ). Progress on this point will be communicated elsewhere.

4. Growth of larger crystals

Let us consider a homogeneous system containing a gelled KDP solution saturated at T_0 which is cooled to a $T_f < T_0$. Obviously for a homogeneous system, the nucleation probability is the same for every point of the system. Therefore, in order to obtain large single crystals, the simple scale-up of the growth cell is not a sufficient condition for success, because of the uncontrolled polynucleation even when seeding is used. Besides this, experiments carried out in our laboratory show that at high crystal growth rates gel is always included during the growth process. Thus, in order to obtain a larger crystal size, we need to produce one point which must later work at a sink of concentration, in such a way that all the supersaturation produced by cooling is consumed by its growth.

The fact that the reduction time for nucleation is much greater for gelled media than for the aqueous solutions can be used to design a device accomplishing the conditions above described, a glass reservoir of 250 cm³ in volume which is covered with a PVC top. The axis of the reservoir is occupied by a cylindric glass column ($\varnothing = 15$ mm) which is attached to the top. A hole in the cover allows a KDP sol saturated at 40 °C to be poured into the reservoir. The device is kept at 40 °C while gelling takes place. Once gelled the reservoir is cooled at 26 °C and the cover and the attached column is carefully extracted. The cilindrical space left by the column is then filled with a water solution of KDP saturated at 26 °C. After one hour, the reservoir is covered

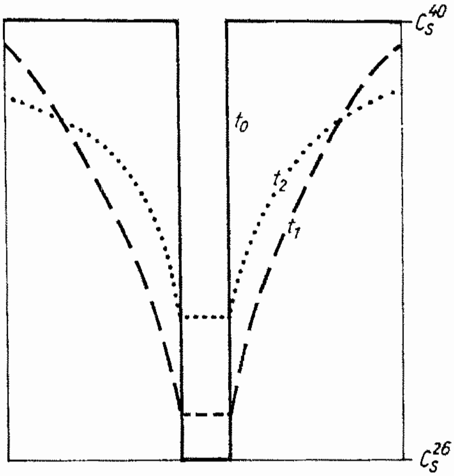

Fig. 4. Plot of concentration gradients in the apparatus for three differents times

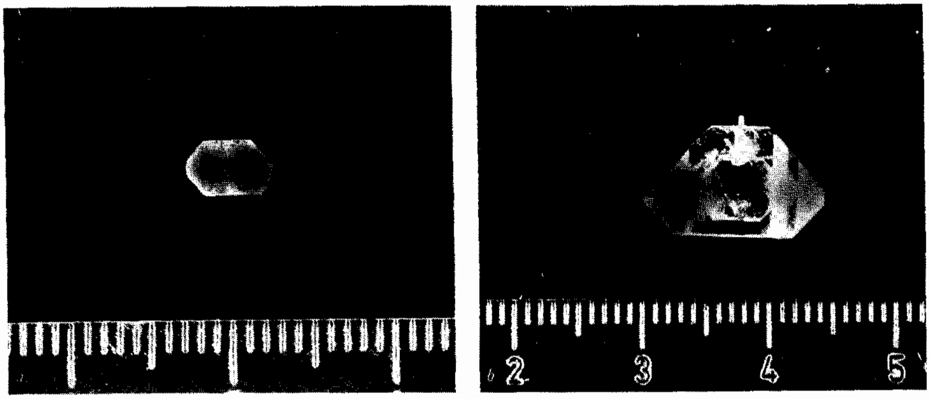

Fig. 5. The seed (a) and the crystal (b) obtained after 48 hours

with another top which, instead of the column, has a glass holder with a KDP seed. In order to avoid nucleation produced by surface evaporation, a thin layer of paraffin is left to float and solidify on the KDP solution. Then, the whole reservoir is maintained at this temperature of 26 °C. Thus, a sink of concentration is created and therefore a diffusion flux from the gel to the seed occurs. Because the nucleation time is higher in gels than in solutions, polynucleation in the gel is avoided and the concentration pattern is ruled by the diffusion flux from the gel to the growing seed as shown in Figure 4. Figure 5 shows the seed and the obtained single crystal after period of 48 hours with a average growth rate along the Z axis of 62 μm/hour.

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