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ON THE GROWTH OF KDP AND KDP:Ni SINGLE CRYSTALS BY THE GEL TECHNIQUE

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ABSTRACT

Kinetic aspects of KDP and KDP:Ni single crystal growth in the gel technique are examined; the growth is controlled by volume diffusion. The growth rates of KDP and KDP:Ni are in the same range as those frequently encountered in industrial crystallization.

KEY WORDS: phosphates, crystal growth

Introduction

The growth of $NH_4H_2PO_4$ (ADP) and KH_2PO_4 (KDP) single crystals in gels has been reported by different authors. Glockber and Soest (1) described the growth of ferroelectric ADP crystals in silica gel by a method which involved reducing their solubility by means of diffusing NH_4Cl. Brezína and Havránková (2) described the growth of KDP single crystals in agar gel, and they decreased the solubility of this compound by using ethyl alcohol. Recently, Joshi and Antony (3) found that silica gels are better than other organic gels for growing KDP crystals, and García-Ruiz and Martín-Vivaldi (4) described the use of a hybrid gel technique for KDP. More recently, Lefaucheux et al. (5) have compared the quality of KDP and ADP crystals grown in tetramethoxylane gels and in solutions by using X-ray topography. They show that growth bands and dislocations are suppressed or reduced bu gelling the growth medium.

Apart from the fact that these ferroelectric compounds are of interest in the field of material science, their chemical properties are highly suitable for the study of kinetic problems associated with the diffusion technique. The aim of this paper is to describe the growth of KDP and KDP:Ni single crystals in a silica gel at pH = 5.5, with special emphasis on the kinetic aspects.

Experimental

Silica gels were produced by acidifying a solution of sodium metasilicate (specific gravity: 1.06 gr/cm^3) with a saturated solution of KDP, up to pH = 5.5. This pH was chosen as an optimum value after previous experiments with different pH values. KDP (Merck G.R.), three times recrystallized (for initial purifiaction purposes), was used in all the experiments. No impurities were found (by optical absorption) in the reagents used for this purpose. Experiments were carried out with two-layer and (mostly) three-layer arrangements (Fig. 1). For the latter, the second layer was made by acidifying a sodium metasilicate solution with (N) acetic acid. After gelling, ethyl-alcohol was placed on top of the solution; it diffuses into the gel, thereby decreasing the solubility of KDP. $NiCl_2 \cdot 6H_2O$ solutions of two different concentrations (0.5%; 0.1%) were used as dopant sources for the growth of KDP:Ni single crystals, added either to the gel layer or to the alcohol layer. The incorporation of Ni is desirable for EPR studies.

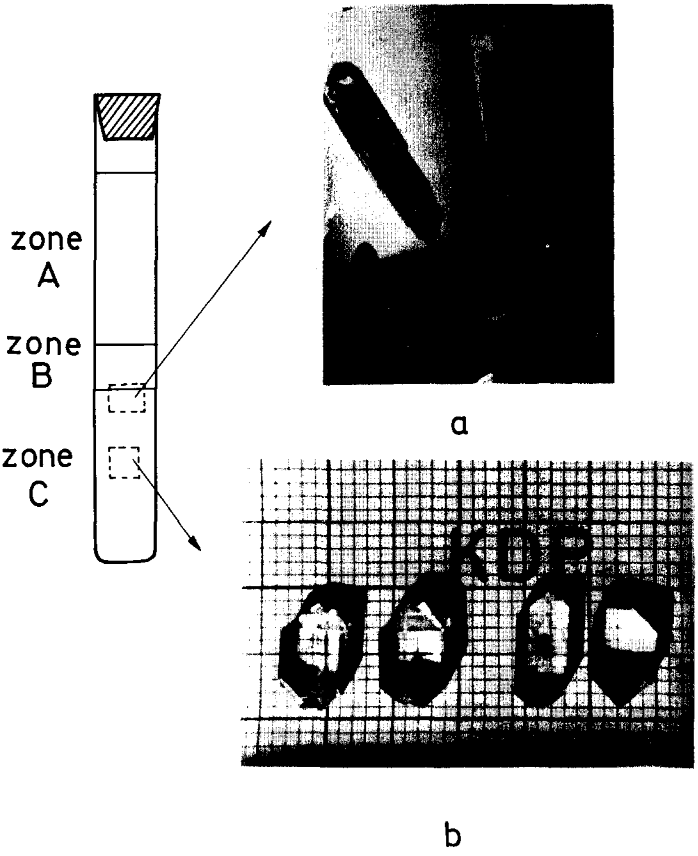

FIG. 1

Schematic three-layer method with (a) an example of dendritic KDP growth and (b) an example of KDP single crystals. (Zone A: ethyl alcohola with or without Ni; Zone B: neutral gel; Zone C: gel and saturated KDP

In order to determine the optimum growth conditions a set of 90 experiments with varying KDP and $NiCl_2 \cdot 6H_2O$ concentrations was carried out. The crystal growth rates were measured by means of a microscope and camera. Pictures were taken at regular intervals, and the distances between opposite [010], [011] faces and [001] poles could be measured with accuracy. The etching behavior of [100] surfaces was also investigated, using an ethanol (25%) and acetic acid mix as etchant (60 second etching times).

Results and Discussion

In the two-layer method, the supersaturation in the zone near to the interphase between the gel and the supernatant solution is very high. Consequently, a few minutes after the supernatant solution is added, nucleation and dendritic growth take place in the gel, and also in the solution as a result of the counterdiffusion of alcohol and KDP molecules. In order to control the nucleation density, the intermediate, neutral gel layer (B in Fig. 1) contained no KDP, but some dendritic growth takes place even then; however, in the main, needles [001] grow down from the interphase layer into the gel containing KDP (Fig. 1). During the earlier stages one finds a large number of fluid and gel inclusions; later these diminish as the crystals become large. At a distance of 1-2 cm from the interface the needles become optically clear, and take the usual KDP habit, prismatic [001] amd pyramidal [101] faces. Good KDP untapered single crystals up to 500 mm^3 were obtained in the middle of column C in Fig. 1. In all the experiments one large KDP crystal appeared in the end zone of the tube (Fig. 2).

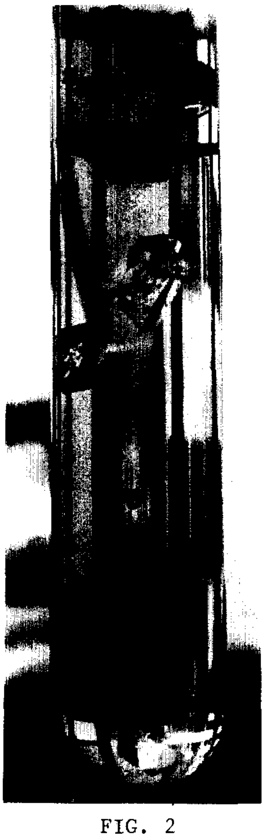

FIG. 2

Example of well-formed KDP crystal observed near the bottom of the growth tube.

When the prism faces of the freshly grown crystals were etched, a small number of elongated parallelogram-shaped dislocation etch pits, similar to those reported by Sangwal et al. (6), were observed. Figure 3 shows their low density. According to Lefaucheux et al. (5), the crystal quality can be improved by lowering the density of the sodium metasilicate solution. However, gels of density lower than 1.06 gr/cm^3 are too brittle and, as growth progresses, the weight of the larger crystals fissures the medium. As a result the crystals fall to the bottom, as shown in Fig. 4. This migration is helped by the initial appearance of cusp-shaped cracks around the crystals (i.e. spaces free of gel-containing solution). The optimization of crystal size therefore calls for (a) the use of a higher gel density which, however, introduces defects during the nucleation and early growth stages, or (b) the use of hybrid gel techniques (4).

FIG. 3

Etch pits in [010] faces after 60 sec. etching-time with 25% ethanol-acetic acid. Scale bar: 0.1 mm.

Representative growth rates, measured as described above, were R_{010} = 18 µm/hr for prism faces [010]; R_{011} = 25 µm/hr for bipyramidal faces [011]; and R_{001} = 30 µm/hr for the c-axis, [001] direction. The following relations are also representative:

$$R_{001}/R_{010} = 1.7; \quad R_{011}/R_{010} = 1.4 \qquad (1)$$

which are similar to those reported by Byeva (7,8) for the growth of ADP from solution at the same pH. They are also within the range of growth rates used in idustrial crystallization processes (9). This finding disposes of one of the crit-

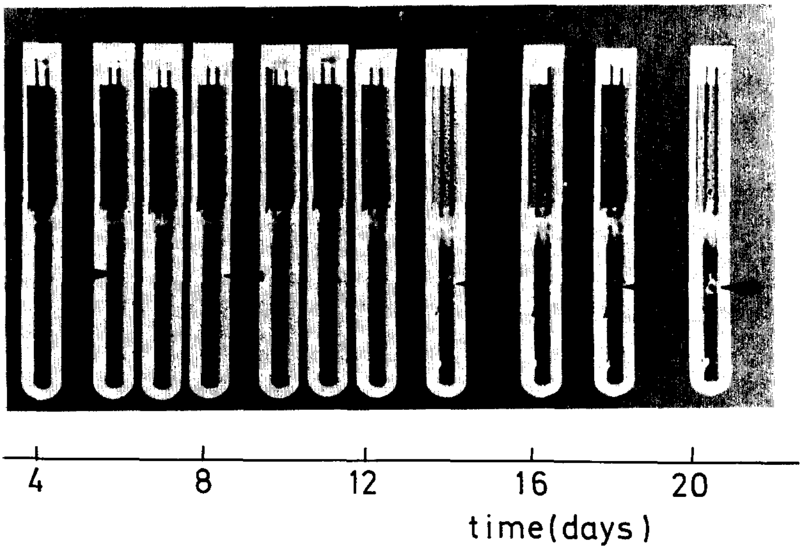

FIG. 4

Physical breakdown of a low density gel; the arrow shows falling crystal as growth proceeds.

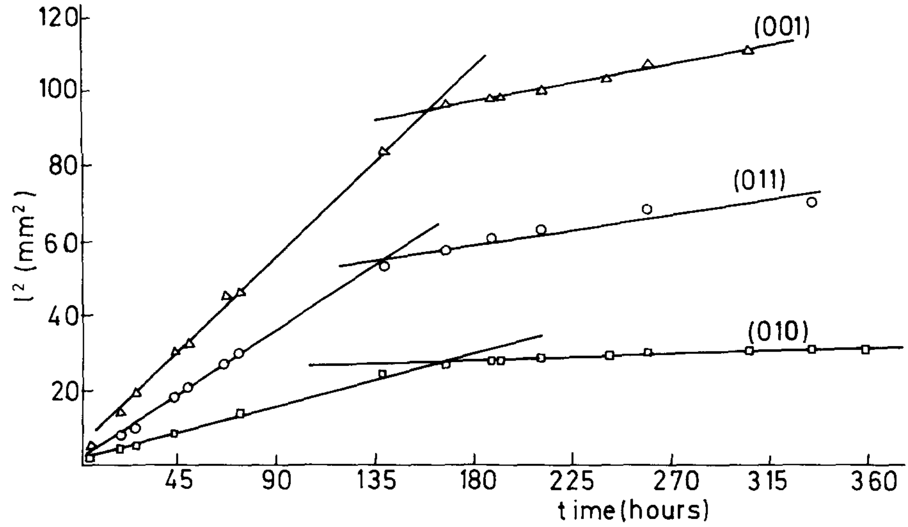

FIG. 5

Typical growth rates for different faces in KDP crystal (run 10'). Time as from the beginning of the first measurement. ℓ = semi-distance between opposite faces.

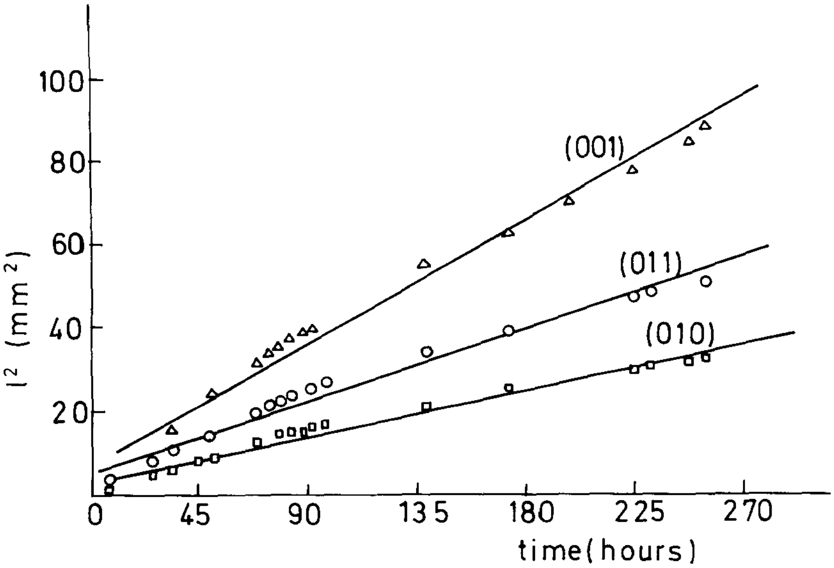

FIG. 6

Typical growth rates for different faces in KDP-Ni doped crystal (run 1'). t and ℓ as in Fig. 5.

icisms commonly levelled against the gel method: that it is too slow. Joshi and Paul (1) have shown that the ratio R_{011}/R_{010} for KDP single crystals grown from solution decreases as the supersaturation increases. For static conditions (i.e. without stirring of the bulk solution), the higher supersaturation (3.5×10^{-2}) investigated by these authors gives a R_{011}/R_{010}value of 1.993. Comparison with the present results suggests that the KDP single crystals grown in a gel system grow at higher supersaturations than those ordinarily grown in solution. Moreover, their crystal perfection is better.

Time-size plots (t versus ℓ^2) are shown in Fig. 5; here t is time in hours, beginning with the first measurement, and ℓ the semi-distance between opposite faces. Linear relationships have been observed in all cases, with correlation coefficients between 0.993 for [001] and 0.986 for [010] surfaces, suggesting that bulk diffusion was the rate-determining process. A tentative explanation of the slope change at about t = 120 hours can be provided by considering the effect of the diffusion zones surrounding neighboring crystals. Due to technical problems, the measurements begin 15 hours after the alcohol solution is poured on the gel. Therefore, the earlier growth stages in which a departure from linearity must be expected are not recorded.

The introduction of Ni into the KDP lattice presents problems during growth from solution by classical methods (i.e. by temperature decrease; isothermal evaporation or transport method). By varying the initial concentration of Ni in the gel-diffusion systems here used (zones C and A in Fig. 1), it was possible to obtain KDP crystals containing between 6 and 10 parts/million of Ni. More Ni was incorporated into the crystals when the Ni source was directly in the gel. However, solutions with more than 0.1% Ni give rise to a green precipitate, as a result of complexing with silica. Ni contents appear to be lower in crystals which were not surrounded by growth veils, for reasons which are still under investigation. The growth rates were similar to those of Ni-free crystals. Figure 6 shows the observed size-time relationships. They exhibit a periodic "ripple" which is believed to be significant. Though further confirmatory work is needed, the ripple is thought to represent a periodicity which is closely related to the phenomena responsible for the formation of Liesegang Rings of sparingly soluble compounds.

Conclusions

The present results show that KDP single crystals can be grown in silica gel at pH 5.5 with growth rates similar to those obtained in industrial crystallization, but the crystal quality of the gel-grown product is higher. Diffusion is the rate-determining process. Ni-doping has also been demonstrated.

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