JOURNAL OF MATERIALS SCIENCE 13 (1978) 939–944

Single crystal growth of ferroelectric potassium dihydrogen orthophosphate in silica gels

M. S. JOSHI, A. V. ANTONY
Physics Department, Sardar Patel University, Vallabh Vidyanagar, 388120, Gujarat State, India

The growth of transparent single crystals of potassium dihydrogen ortho-phosphate (KDP) in silica gels up to 40 mm x 8 mm x 7 mm in size is reported. A brief description of the material preparation, growth procedure and crystal characterization is given. Studies of the effects of pH and gel ageing upon the quality and nucleation of crystals are also reported. With an initial gel pH of 5.1, some crystals grow initially in the form of needles, while subsequent growth leads to bigger crystals, Cusps are observed around some of the growing crystals. Microstructures of the habit faces of gel grown crystals are explained.

1. Introduction
The KH_2 PO_4 group of compounds have gained considerable interest in the field of materials science on account of their extremely interesting ferroelectric, piezoelectric, pyroelectric and electro-optical properties. Extensive work has been carried out on the material since the ferroelectric property was first reported by Busch *et al.* [1]. A substantial amount of information is available on the nucleation and growth of KDP crystals [2, 3] from aqueous solution. Recently an attempt was made by Brezina *et al.* [4] to grow KDP crystals from agar gel while Glockber *et al.* [5] made another attempt to grow ADP, its isomorphous salt, from silica gel.

Several investigators [6, 7, 8] have used the gel technique for growing perfect and transparent single crystals. Although the technique is an old one a renaissance in the field has occurred with the work of Henisch *et al.* [9, 10, 11]. Gel growth, on the other hand, is also attractive because of its simplicity and the quality of crystals produced.

In the gel growth of crystals generally two or more species are reacted to form the desired solid product. Good single crystals are obtained by suitable adjustments of concentration, pH and temperature of the solutions. In the present study use is made of the method of Glockber *et al.*[5] for the preparation of the gel. KDP was incorporated inside the silica gel and was crystallized out by adding alcohol.

In this study, it was found that silica gels are better than other organic gels for growing KDP crystals due to better crystallinity of the product in the gel. The present paper reports the best conditions for growth of large transparent single crystals of KDP in gels and the effects of altering the parameters affecting the nucleation and growth of such crystals. Observations made during growth are also reported.

2. Experimental
The gel was prepared from an aqueous solution of sodium metasilicate (sp. gr. = 1.06) by acidification with saturated solution of KDP at 30° C. AnalaR grade (BDH, India) KDP powder, doubly distilled water and dehydrated absolute alcohol were used. Test tubes, beakers and U-tubes were employed as cystallization vessels. However, the best results were obtained in test tubes (1 inch diameter and 1 foot long) with a gel pH of 5.3. After the gel was set an equal volume of ethyl alcohol was added slowly above the gel and the test tubes were tightly sealed with rubber corks to

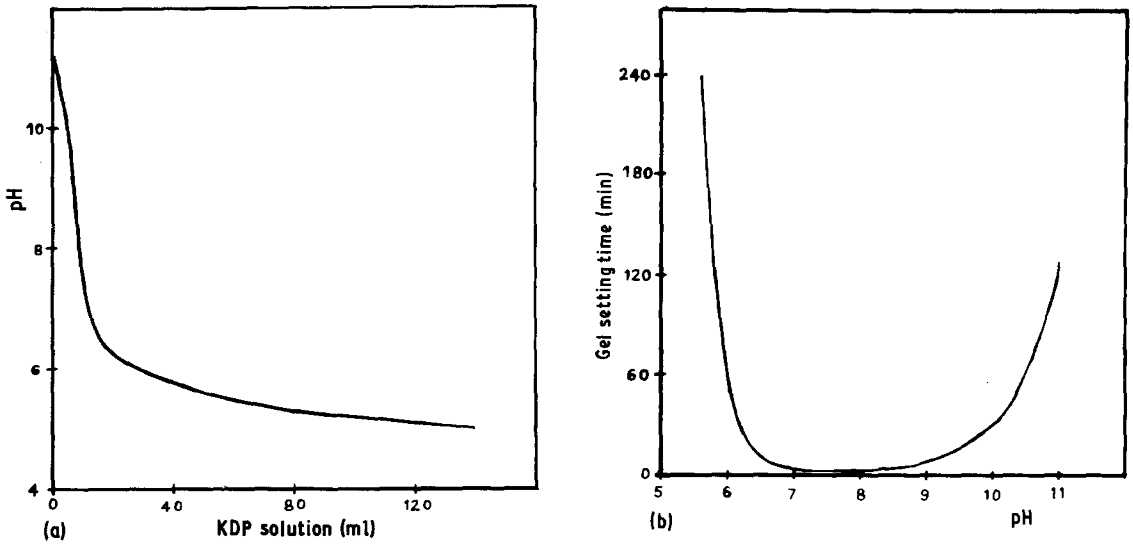

Figure 1 (a) A plot of the variation in gel pH with the addition of 2.5 M KDP soludion to 20 ml of sodium metasilicate solution of sp. gr. 1.06 at 32° C. (b) A plot of gel setting time against pH of the gel mixture at 30° C.

prevent evaporation of alcohol. Alcohol reduces the solubility of KDP, which first precipitates at the gel–alcohol diffusion interface. Diffusion of alcohol into the gel was followed by formation of nuclei which then grew larger. Fig. 1a illustrates the variation in pH with the amount of KDP solution (2.5 M) added to 20 ml of sodium metasilicate solution at 32° C, while Fig. 1b shows a plot of gel setting time against the pH of the solution.

The present method yielded crystals up to 40 mm x 8 mm x 7 mm in size, some of which are shown in Fig. 2. Completion of crystallization took about three to four weeks.

3. Observations and discussion

3.1. Nucleation control

The usual two-layer method schematically represented in Fig. 3a produces a large number of nuclei near the diffusion interface. To overcome this difficulty the following methods were used for nucleation control: (a) An intermediate gel column of the same material with a low concentration, as shown in Fig. 3b, was tried. Here the nucleation control depends upon the length and density of the intermediate gel column. However, it did not enhance the size of the crystals. (b) Acetic acid was used for the intermediate gel

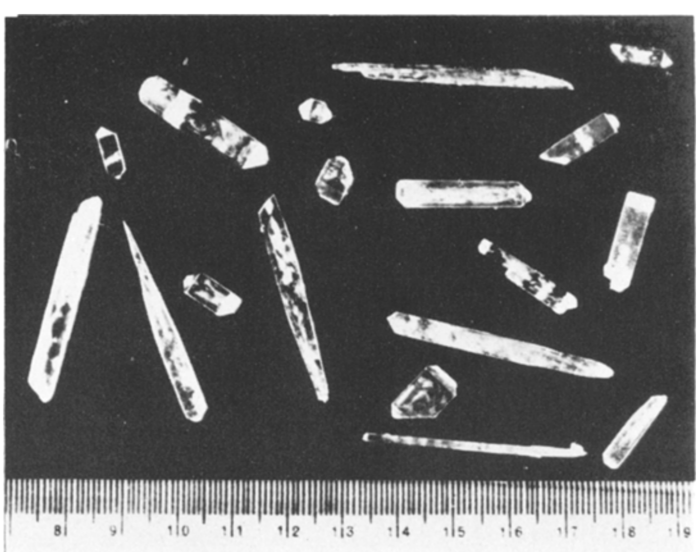

Figure 2 A photograph of some of the crystals grown in gels.

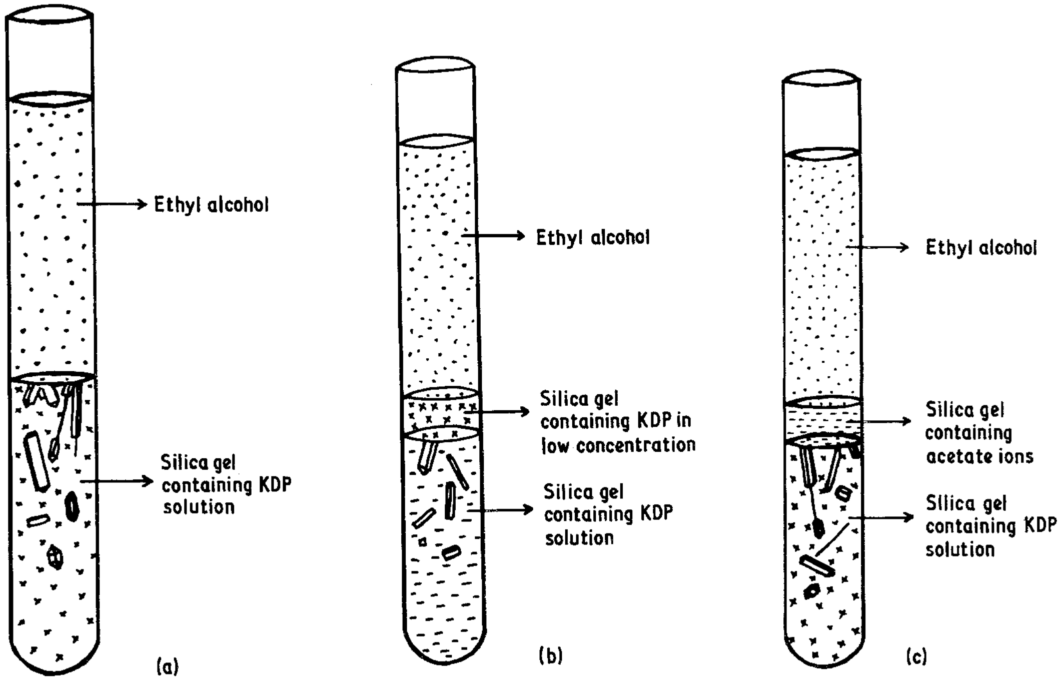

Figure 3 Schematic representation of the two-layer method adopted and the three-layer methods used for nucleation control.

column as shown in Fig. 3c. This system effectively controlled the nucleation and also yielded larger transparent single crystals.

3.2. Effect of pH and gel ageing

To investigate the effect of pH of the gel on the growth of KDP crystals, gels of different pH values ranging from 5.1 to 6.2 were tried. Higher pH values gave denser gels, which in turn yielded poorer crystals and reduced the number of nucleation centres.

According to Henisch *et al.* [11] gel ageing reduces the cell size and consequently the rate of diffusion of the material into the gel. In the present work gels with pH 5.3, when allowed to age for different periods before being covered with

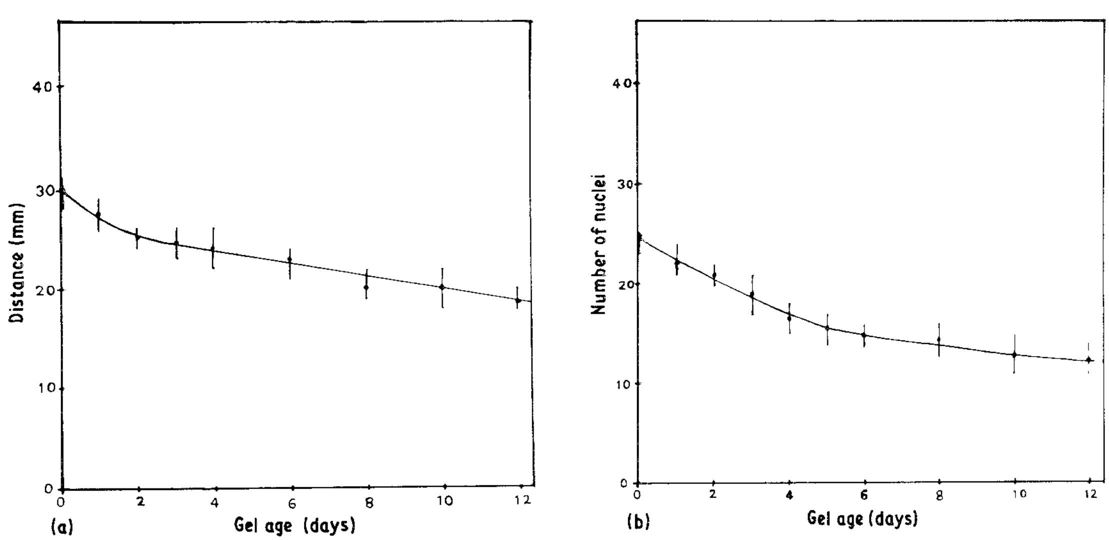

Figure 4 (a) A plot of the advance of precipitation front against gel ageing after two weeks of addition of alcohol. (b) The number of nuclei produced versus gel age.

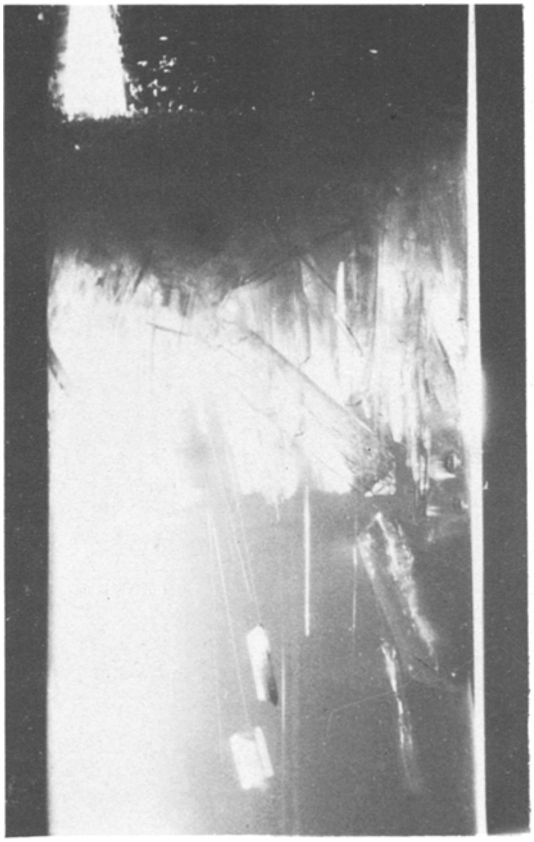

Figure 5 KDP crystals growing in the form of needles; pH 5.1.

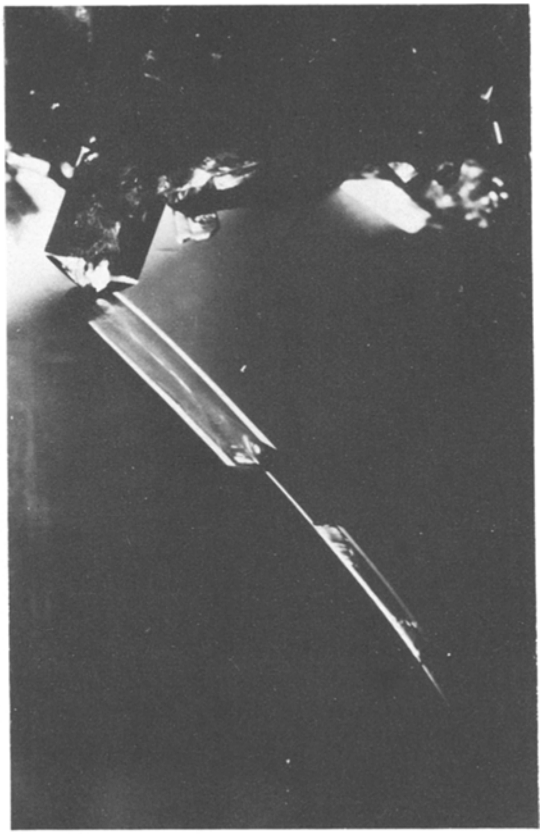

Figure 6 Lateral growth taking place along one of the needles after the needle growth has stopped.

alcohol, showed a gradual decrease in the number of nuclei with the ageing. Fig. 4a is a plot of distance of precipitation front from the diffusion interface (which in turn is a function of rate of diffusion of alcohol into the gel) against the gel ageing (after a lapse of 2 weeks after adding alcohol). A graph of the number of nuclei against gel age is shown in Fig. 4b.

It may be noted that with the increase in the distance from the gel–alcohol interface the number of crystals growing decreases but their transparency increases. It is suggested that this is due to the lower supersaturation and consequently lower growth rate of crystals deep inside the gel as compared to that near the diffusion interface.

3.3. Formation of needles

In a large number of cases it was found that at pH 5.1 needle-shaped crystals grow along with other crystals as shown in Fig. 5. These needles (about 0.5 mm in thickness) first grow along their length and reach a certain maximum size (4 cm was the longest observed) in about 4 to 6 h. This is followed by growth at nuclei at several points along the needle (see Fig. 6) and the crystals now extend more along the needle than at right angles to it, leaving gaps in which no growth takes place. Finally, the growth takes place in such a way that the crystal shown in Fig. 6 assumes the form shown in Fig. 7.

3.4. Cusp formation

When a crystal is growing inside a gel the latter is displaced by or incorporated into the former. Formation of cusp-shaped cracks around growing crystals in the gel has been reported by Hanoka [12]. These cusps are found filled with the solutions of the growing cystal. Fig. 8 shows such cusps observed around some of the KDP crystals growing in the gel. It may be noted that such crystals surrounded by cusps are more transparent than those without cusps.

3.5. Characterization

Crystals grown by the gel method exhibited the normal habit, a tetragonal prism in combination

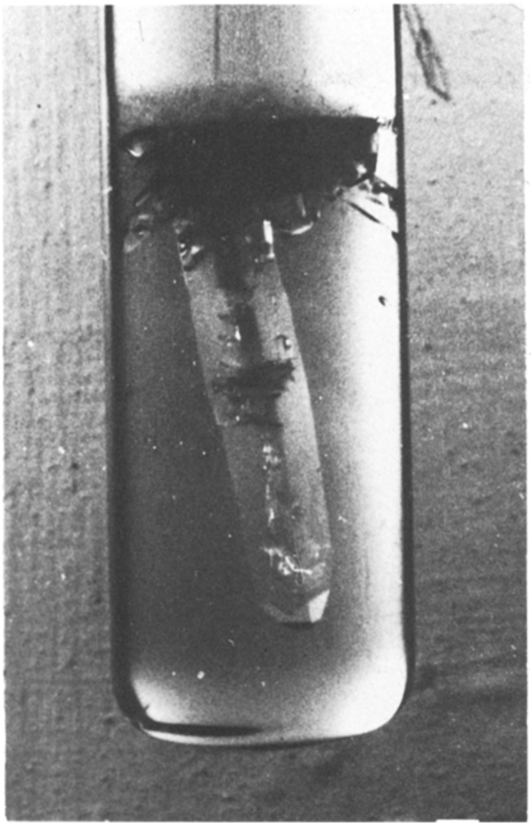

Figure 7 Final stage of the needles in Fig. 6 which have grown to a bigger crystal.

Figure 8 Cusp-shaped cracks surrounding a growing KDP crystal in gel.

with a tetragonal bipyramid. The chemical analysis, X-ray powder diffraction patterns and infra-red spectra proved that the material of the crystal grown is KDP.

3.6. Microstructures

Habit faces of crystals grown by the method described above were examined under a metallurgical microscope. A number of rectangular and square growth hillocks were observed on {0 1 0} prism faces. Density of these hillocks varies at different regions of the crystal face. Sometimes the rectangular and square growth hillocks join to form zig-zag patterns. Some {0 1 1} habit faces of these crystals showed the presence of triangular pits oriented in the opposite sense to the outline of the face.

4. Conclusions

Silica gels are found as good media for growing good quality crystals of KDP. Transparent single crystals of KDP up to 40 mm x 8 mm x 7 mm in size have been grown for the first time in silica gels. Nucleation control can be obtained with an intermediate gel column. Transparency of the crystals depends on the pH of the gel. Ageing of the gel supresses the number of nucleation sites in the gel. Some crystals are found surrounded by liquid while they grow, as is evident from the cusps observed. Observations of layer-structured growth hillocks and lateral growth along the needles are evidence of a two-dimensional nucleation process for the growth and developement of KDP crystals.

Acknowledgement

One of us (AVA) wishes to express his thanks to C.S.I.R., Goverment of India, for financial assistance during the course of this work.

References

1. G. BUSCH and P. SCHERRER, *Naturwiss 23 (1935)* 737.
2. J. W. MULLIN and A. AMATAVIVADHANA, *J. Appl. Chem.* **17** (1967) 151.
3. M. S. JOSHI and BABY. K. PAUL, *J. Cryst. Growth* **22** (1974) 321.

4. B. BRENZINA and M. HAVRANKOVA, *Mat. Res. Bull.* **6** (1971) 537.
5. D. A. GLOCKBER and J. E. SOEST, *J. Chem. Phys.* **51** (1969) 3143.
6. H. K. HENISCH, J. DENNIS and I. J. HANOKA, *J. Phys. and Chem. Solids* **29** (1955) 493.
7. Z. BLANK and W. BRENNER, *Nature* **222** (1969) 79.
8. A. F. ARMINGTON and J. J. O'CONNOR, *J. Cryst. Growth* **3, 4** (1968) 367.
9. H. K. HENISCH, J. DENNIS and I. J. HANOKA, *J. Electrochem. Soc.* **112** (1965) 627.
10. J. DENNIS, H. K. HENISCH and P. CHERIN, *ibid* **112** (1965) 1240.
11. H. K. HENISCH, "Crystal Growth in Gels" (The Pennsylvania State University Press, University Park, Pennsylvania, 1970) p. 93.
12. I. J. HANOKA, *J. Appl. Phys.* **40** (1969) 2694.

Received 14 June and accepted 13 September 1977.