CHAPTER - 3

GROWTH OF SINGLE CRYSTAL OF POTASSIUM DIHYDROGEN PHOSPHAT

3.1 INTRODUCTION:

The KH_2PO_4 group of compounds have gained great interest in the field of material science on account of their extremely interesting ferroelectric, peizoelectric, pyroelectric and electrooptic properties. A substantial amount of information is available on the nucleation and growth of large KDP crystals from aqueous saturated solution[1,2]. The large KDP crystals were grown from solution by rotating fluid method. This technique is difficult and accurate temperature regulation is needed. Extensive work has been carried out on the material since the ferroelectric property was first reported by Busch et al[4]. 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[5] described the growth of ferroelectric ADP crystals in silica gel by a method which involved reducing their solubility by means of diffusing NH_4Cl. Brezina and Havrankova[6] described the growth of KDP single crystals in agar gel, and they described the solubility of this compound by using ethyl alcohol. Recently, Joshi and Antony[7] found that silica gels are better than other organic gels for growing KDP crystals, and Garcia - Ruiz and Martin - Vivaldi[8], described the use of a hybrid gel technique for KDP more recently.

Lefaucheux et al[9] have compared the quality of KDP and ADP crystals grown in tetramethoxylane gels and in solutions by using X-ray topography. Since these crystals are highly soluble in water (solubility of KDP 20.04 A (wt%) at 25°C), single crystal growth in gels at near ambient temperature is an alternative method to obtain these crystals. Traditionally, this type of growth involves a chemical reaction in the gel between two soluble reactants to form an insoluble product. In the present method, advantage is taken of the tendancy of ethyl alcohol or reducing the solubility of KDP. The technique or the experimental method can be described as crystal growth by reduction of solubility.

3.2 EXPERIMENTAL AND OBSERVATION:

The various crystallization vessels used in the present work were :

i) Test tubes of 2.5 cm outside diameter and 20 cm. length,

ii) 100 ml., 250 ml. and 1000 ml. beakers. The chemicals used for growing these crystals were :

1) Na_2SiO_3 powder (Ramoli)
2) Analar grade KDP powder (BDH India)
3) Doubly distilled water
4) Dehydrated absolute ethyl alcohol.
5) Cobalt nitrate (BDH Analar grade)
6) Nickel chloride (BDH Analar grade)

The Silica hydrogel was used as the growth media throughout the experimental study. Firstly the sodium silicate stock was

solution was prepared. The weight percent of this solution was adjusted to 50. The solution was kept away from the contact with the atmosphere to avoid absorption of CO_2 for some 15 to 20 days. When most of the impurities were settled down, it was transferred into another beaker. This process was repeated till a transparent sodium silicate was obtained. Required concentration of this solution was obtained by dilution method. 30 ml. of saturated solution of KDP (2.5M) was added to 25ml. sodium metasilicate of 5 wt.% at room temperature. The gel was set within 1 to 2 days. Then it was left for another 12 hours to set properly. After setting of the gel an equal volume of ethyl alcohol was added slowly above the gel so that there should not be any gel surface damage. And then the test tubes were sealed with rubber corks to prevent evaporation of ethyl alcohol. This decreases the solubility of KDP, which precipitates in close vicinity of the diffusion interface of alcohol and gel, later in the bulk of gel. Diffusion of ethyl alcohol into gel was followed by formation KDP nuclei which then grow larger in size. Fig. 2 shows crystals growing in silica gel.

Crystals were formed near the diffusion interface in the gel and also within the gel. The nuclei produced near the diffusion interphase were larger in number and smaller in size, where as crystals formed in the bulk of the gel column were larger in size.

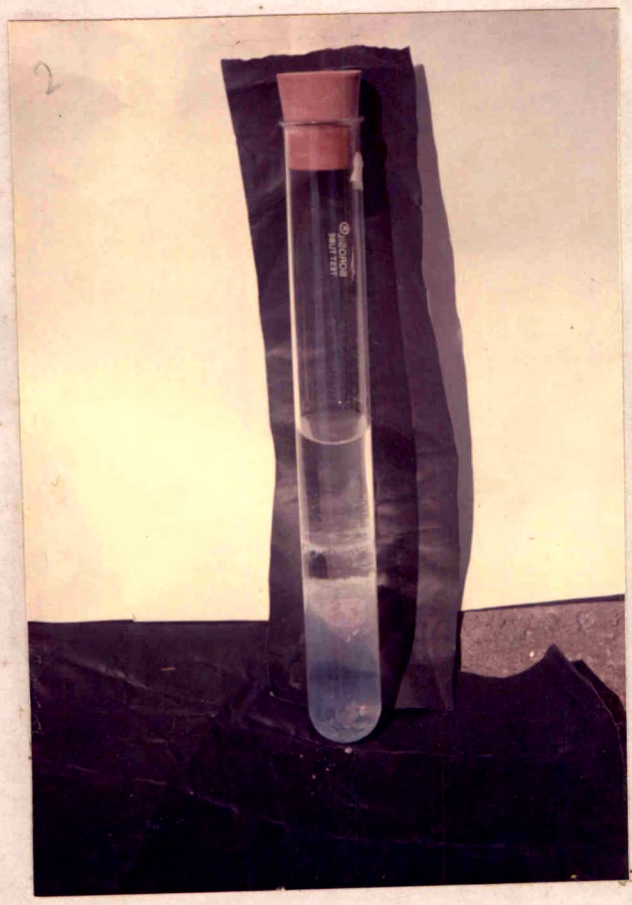

Fig. 2

This procedure yielded the crystals of maximum size of 20 x 8 x 5 mm^3 with pH 5.5 and gel density of 5 wt. %.

3.3 RESULT AND DISCUSSION:

1. Effect of pH --

The pH values of gels were varied from 5 to 7. Good crystal were observed at a pH of 5.5 gels. At higher densities excess of sodium ions were present and gels were not transparent. There was an inclusion of SiO_2 in some crystals as shown in fig 3. This may be due to the improper cell formation at higher pH values of gels.

At low pH values gels were not set properly. This may be due to incomplete formation of silica gel, as at low pH values the tendency towards chain formation decreases.

Best crystals in terms of transparency, inter crystalline seperation were obtained at pH value of 5.5. The transparent single crystals are shown in fig. 4.

2. Effect of gel density -

The gels of different densities were obtained by adding 25ml. sodium silicate from 4 wt.% to 7 wt.% to 30 ml. KDP (2.5M) solution, keeping pH constant at 5.5.

At very low densities, gels were not set. At very high

Fig. 3

Fig. 4

gel densities, the gels were not transparent and contamination of crystals with silica gel was also observed to increase. And as the dense gels have small pore sizes. The nuclear density was found to be decrease. The gel density of 5 Wt.% was found to be the best for growing better crystals. The grown crystals were found to be having different habits as shown fig. 5. Also in some cases twinning was also observed as shown in fig. 6.

3.4 GROWTH OF KDP : Ni AND KDP : CO CRYSTALS:

Doping can easily be achieved by adding the dopant to the gel or supernant reagent in solution forms. A variety of doped crystals can be produced. Because of doping coloured crystals also can be obtained.

Recently J. M. Garcfa - Ruiz et al[10] described the growth of KDP and KDP : Ni single crystals by the gel technique. More recently NH_4PO_4 mixed crystals from gel medium were also grown.

3.5 EXPERIMENTAL:

Silica hydrogels were produced by acidifying a solution of sodium metasilicate (weight percent 5) with a saturated solution of KDP (2.5 M) upto pH 5.5. This pH was chosen as an optimum value after previous experiments with different pH values. In all experiments KDP (analar grade) two time recrystallized (for initial purification purposes) was used. Cobalt nitrate solutions of different

Fig. 5

Fig. 6

concentrations varying from 0.1 to 1.0 of weight percent were prepared. And were used as doping sources for the growth of KDP : CO single crystals. After setting of the gels, the alcohol was added on the top of the gel surface without any damage. The dopant solutions were added to the alcohol layer.

Nickel chloride solutions of two different concentrations (8 wt% and 10 wt%) were used as dopant sources and were added to the gel layer in order to grow KDP : Ni single crystals. The incorporation of impurities is desirable for the lattice parameter studies and dielectric studies.

In the two-layer method the nucleation density in the zone near to the interphase between the gel and the supernant solution was very high. It might due to higher concentration gradients. In the earlier stages a large number of fluid and gel, inclusions were observed. But later as the crystals became large, these were found to be diminished. At certain distance from interphase some niddles were observed. Good KDP crystals were obtained in the middle of the column due to the lower concentration gradients. Fig. 7 shows grown KDP crystals doped with cobalt nitrate in silica hydrogel.

3.6 RESULT & DISCUSSION:

Because of different concentrations of doping source, crystals of slightly different colours were observed. When 0.1% by weight

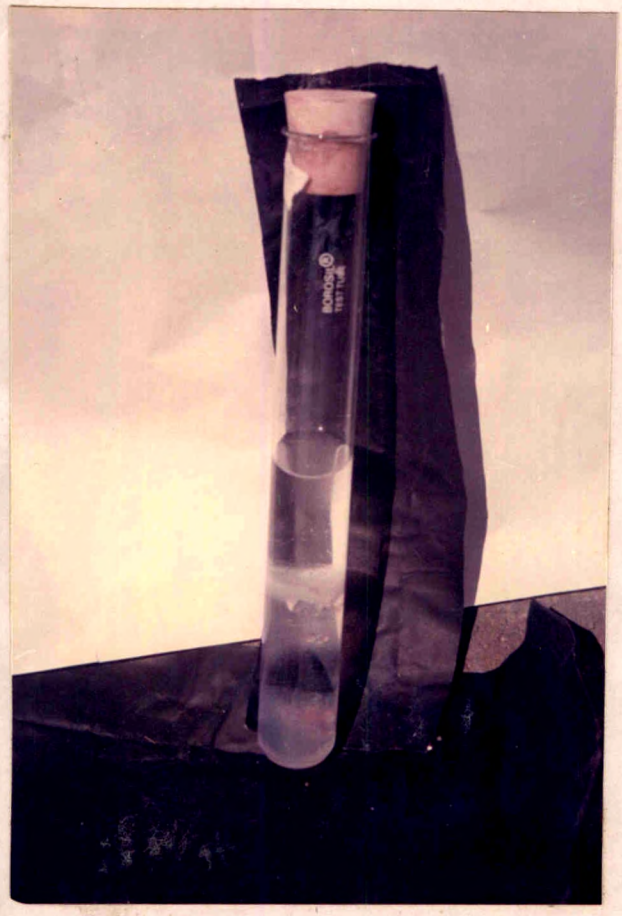

Fig. 7

cobalt nitrate solution, used as a dopant solution, was incorporated inside the gel forming solution, the gel was found to be transparent As the concentration of the impurities were increased, the transparency of gels were found to be decreased. The gels were found be having pinkish colour.

In case of nickel because of the higher concentrations (10wt% and 8Wt%) gels were not transparent. After 1 of 2 days some precipitation was found at the bottom of the tube.

3.7 CONCLUSION:

The best KDP pure crystals produced during this phase of study are clear, solid, uniform in composition, of good purity and show no evidence of inclusions.

KDP single crystals doped with Ni and cobalt can be grown in silica hydrogel at pH 5.5 and density 5 by weight percent. The doped crystals are not transparent. It might be due to absorption of the host lattice.

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