CHAPTER 5

GROWTH OF SINGLE CRYSTA OF NaCl IN SILICA GEL

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5.1 INTRODUCTION

It has already been reported that a variety of solid state experimentation can be grown in silica gel [1,2]. The gel method is especially useful for substances which, because of their low solubilities or low dissociation temperatures or both as in this case, can not readily be grown by other methods. The problem of nucleations of the gel method, because the crystals growing in a gel compete with one another for the solute atoms this competition limits their size and perfection. It is therefore obviously desirable to suppress nucleation centres until only a few crystals are formed. Patel and Rao [2] in a recent review have covered the existing information on the growth of single crystals in gels. But these reports have not described detailed studies on the growth of sodium chloride crystals. The present chapter describes detailed studies on the gel growth of sodium chloride single crystals.

Eventhough the ionic diffusion and velocity are slowed down by the soft three dimensional gel framework, yet this suppressed nucleation rate is also much more than the one required for limited nucleation. Hence nucleation control in gels is one serious problem facing a crystal grower [3] . Attempts to decrease the nucleation sites and enhance the size of the crystals using concentration programming have been found to be tedious and time consuming [4,5]. It is the primary purpose of this chapter to demonstrate the technique of nucleation control in gels using various acid impurities in order to obtain larger and more perfect single crystals of NaCl.

5.2 CRYSTAL GROWTH

The crystallization apparatuses used in the present work were i) test-tubes of 2.5 cm outer diameter and 20 cm length, ii) 250 ml beaker, iii) U-tube of 2.5 cm outer diameter and 30 cm length, iv) beaker-single tube system.

Silica gels were prepared by mixing sodium silicate [specific density 1.02 gm^3] with the required quantity of 1N acetic acid. To this sol saturated solution of sodium chloride was added [6,7]. Analytical reagent grade (BDH) chemicals and doubly distilled water were used through out the present work. The experiments were performed at ambient temperature. pH values of gel were adjusted from 4 to 7 by varying adding a few drops of additional acetic acid.

In the test tubes and beakers, silica gels were prepared by mixing NaCl to a sodium silicate. After setting the gels, feed solutions of Ethanol absolute [ethyl alcohol] were added. In the U-tubes, beaker-single tube system, the gels were prepared by adding acetic acid into the sodium metasilicate. After the gels were set the feed solution ethyl alcohol and sodium chloride were added to initiate crystallization Figures 5.1(a) and (b) show the growth of NaCl crystals in silica gel. It is clearly seen from the figures that the NaCl crystals are not transparent and also not well defined. Therefore, in order to obtain transparent and well defined NaCl crystals, incorporation of various acid impurities in the feed solutions have been tried.

5.3 EFFECT OF IMPURITIES

It has been found that there is a large amount of variation in nucleation density as a function of addition of various types of mineral acids such as H_2SO_4, HNO_3, HCl, $HClO_4$ and salts such as $Pb(NO_3)_2$. The concentration of all the acids and $Pb(NO_3)_2$ were varied from 1 to 4N and the amounts were varied from 4 to 10 ml. The effect of addition of HNO_3 and HCl acid impurities is shown in Figures 5.2(a) and (b). It has been found that as the concentration of acid impurities is increased the total number of the crystals decreased. It is clear from the Figures 5.2(a) and (b) that although the crystals developed of well defined habits but they are almost opaque. It has been observed that at the gel-feed solution interface precipitates formed and below the interface some crystals followed by only a few crystals at greater depths in the gels. This is due to the fact that at the interface the speed of the chemical reaction is fastest and below the interface the concentration gradients decreases with the distance. In the case of $Pb(NO_3)_2$ impurity, the number of crystals are more and they are not well defined which may be due to the formation of lead perchlorate particle clusters.

As far as the $HClO_4$ acid impurity is concerned, this impurity resulted in transparent and well defined NaCl single crystals as shown in Figure 5.3. This is due to the fact that increased solubility of NaCl in perchloric acid. It has been observed that as the normality of the perchloric acid increases, the number of crystals decreases.

Both a high solubility and low supersaturation are desirable in order to produce sites this should be true whether heterogeneous or homogeneous nucleation is involved [8]. A relatively high solubility is also desirable for growing better quality and larger single crystals. Firstly, it provides an example supply of feed material for the growth of larger crystals; secondly it provides a high degree of order; an ion or molecule deposited out of place in the crystal lattice will have more chance of being dislodged and finding its way to a correct site. Thirdly, the degree of saturation is more easily controlled at high than the low solubilities, the solubility here discussed is not aqueous solubility but the solubility of sodium chloride in the presence of acid impurities. This solubility can be altered by controlling the amounts or normalities or both, and many materials which are commonly considered to be insoluble are actually soluble under conditions which can be established in gel growth system.

A saturated solution of NaCl in silica gel and 5 ml of 2N $HClO_4$ in ethyl alcohol feed solution is necessary for the best NaCl crystal growth interms of transparency and intercrystalline seperation. Good quality single crystals have been found to grow in a region of 2 to 5 cm distance from the gel-solution interface, where the supersaturation is moderate.

In the gel volume nearest to the gel-solution interface, crystals formed during the initial growth process have been found to dissolve after 8 to 10 days and well defined good quality single crystals grew in the interior parts of the gel.

5.4 CONCLUSIONS

Good quality transparent and well defined single crystals NaCl have been grown in silica gels using the reduction of solubility method and by adding acid impurities. Out of all the acids, $HClO_4$ has been found to give rise to the best quality NaCl single crystals in terms of transparency and intercrystalline seperation. The impurities reduced the nucleation density and increased the size of the crystals. The method of adding impurities for better quality crystal growth can be tried for other important crystals (like PbS, CdS, ZnS, $CaCO_3$) which could not be properly grown in gels, due to a large number of nucleation centres and also sometimes due to precipitation.

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