Kristall und Technik	15	10	1980	1115–1121

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Growth of Single Crystals of NaCl in Gels

The growth of transparent single crystals of sodium chloride (NaCl) in agar and silica gels up to 4 × 4 × 4 mm size is reported. A brief description of the material preparation, growth procedure and crystal nucleation is given. Hydrochloric acid was used to crystallize NaCl incorporated in the gel which reduces the solubility of NaCl in the gel media. Crystalline perfection has been studied using the chemical etching method.

Es wird über das Wachstum von transparenten NaCl-Kristallen (bis zu 4 × 4 × 4 mm Größe) in Agar- und Silicagel berichtet. Dazu erfolgt eine kurze Beschreibung der Materialvorbereitung, des Wachstumsvorganges und der Keimbildung. Chlorwasserstoffsäure verringerte die Löslichkeit von NaCl im Gel. Die Kristallperfektion wurde mit Hilfe des chemischen Ätzens untersucht.

1. Introduction

It has been reported (HENISCH et al.; PATEL, BHAT; ARMINGTON, O'CONNOR) that a variety of crystals suitable for research and technology can be grown in gels. The method is specifically useful for substances which because of their low solubilities or low dissociation temperatures, cannot readily be grown in other methods. The gel medium prevents turbulence and remaining chemically inert, provides a three dimensional structure which permits the reagents to diffuse at a desirable controlled rate. Further, its softeness and the uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth. Even though crystals of a large number of substances including metals (LIAW, FAUST; KRATOCHUIL, SPRUSIL) and highly water soluble substances such as KDP (BŘEZINA, HARVANKOVA) and ADP (GLOCKER, SOEST) have been grown, it appears that no efforts have been made to grow alkali halide crystals gels. The present paper describes the growth of NaCl single crystals in agar and silica in gels for the first time. The nucleation, growth, habit and perfection studies of NaCl single crystals have also been reported.

2. Experimental and observations

2.1. Crystal growth

The technique of (GLOCKER, SOEST) employed for the growth of ADP crystal was used here. NaCl solution was incorporated in the gel medium and HCl acid solution of various concentrations was added above it. As the acid diffuses into the gel medium, crystals were formed in the gel and the growth takes place at low pH.

The agar and silica gels were used as the growth media throughout this study. The gel was prepared by mixing agar and pure sodium silicate solution with the required amount of HCl acid. The crystallization apparatus used in the present study was a glass test tube of 2 to 3.5 cm diameter and 25 cm long. Analytical reagent grade chemicals and double

distilled water were used throughout this study. Completition of crystallization (with crystal size upto 4 × 4 × 4 mm) took about 10 to 20 days. The results are based on the statistical average of five sets of experiments.

2.2. Growth procedure in Agar gel

The agar-gel was prepared as follows. Firstly, a saturated solution of NaCl at room temperature was prepared, then agar agar powder (the amount was so chosen to have the required gel density) was added to the saturated NaCl solution and heated to 70 °C for about 10 minutes to get it dissolved. The solution was filtered and allowed to cool in test tubes. The gel sets as it cools to room temperature. Then a solution of HCl acid was poured on the top of the gel. The concentration of HCl solution varied from 2N to 10 N. Figure 1a shows crystals of NaCl growing inside the tube, while figure 1b illustrates some typical crystals of NaCl grown in the present work.

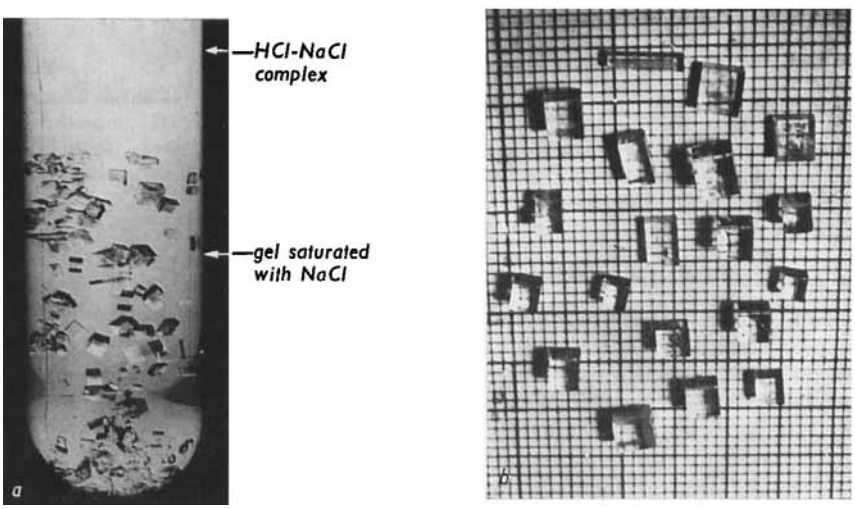

Fig. 1a) NaCl single cystals growing in Agar gel; b) Some of the typical NaCl crystals grown in Agar gel

2.3. Growth procedure in silica gel

Silica gel was prepared by adding 1 N HCl acid to an aqueous solution of sodium metasilicate of specific gravity 1.04 until the pH comes to about 4. Now, NaCl powder was dissolved in the above solution until it got saturated. The mixture was allowed to set in test tubes. The setting time was found to vary with pH of the gel media. After the gels were set, the feed solution of HCl acid of various concentrations was placed above the gels. (For HCl acid of normality less than 5.5 should be saturated with NaCl, before feeding the acid on the top of the gel). Diffusion of the HCl acid to the gel was followed by the formation of nuclei which later grows to bigger sized. Crystals growing by this method are shown in Figure 2a and Figure 2b shows some typical crystals of NaCl. For both the methods, important experimental details and growth parameters are summarized in Table 1.

It may be noted that:

1. The preparation of the agar gel was more simpler than the silica gel.
2. The growth rate in agar gel is higher compared to the growth rate in silica gel.

Table 1
Growth parameters of growing NaCl Single Crystals

Particulars of gels	density of gel	Concentration of HCl acid added over the set gels	growth period	size of the grown crystal	habit of the grown crystals	quality of the crystals
Agar	7.5 gm/ litre	2 N	—	no crystal	—	—
		4 N	15 days	4 × 4 × 4 mm	Equant, bladed tabular and accicular	very good
		6 N	10 days	3 × 3 × 3 mm	cubic	good
		8 N	5 days	2.5 × 2.5 × 2.5 mm	cubic	poor
		10 N	2 days	2 × 2 × 2 mm	cubic	poor
Agar	5.0 gm/ litre	2 N	—	no crystal	—	—
		4 N	10 days	3 × 3 × 3 mm	cubic	very good
		6 N	5 days	2 × 2 × 2 mm	cubic	good
		8 N	2 days	2 × 2 × 2 mm	cubic	poor
Silica	1.040 gm/cc	2 N	—	no crystal	—	—
		4 N	30 days	3 × 3 × 3 mm	cubic	very good
		6 N	30 days	4 × 4 × 4 mm	cubic	very good
		8 N	30 days	3 × 3 × 3 mm	cubic	good
		10 N	30 days	—	Hopper	poor
		11.3 N	30 days	—	Dendrite	poor

3. Due to less dissolution of agar gel in HCl acid, the maximum growth period for crystals in agar gel was about 15 days. But in silica gel growth can be continued for a period of 30 days.

4. Size and the quality of the crystals were found to be better in silica gel compared to agar gel.

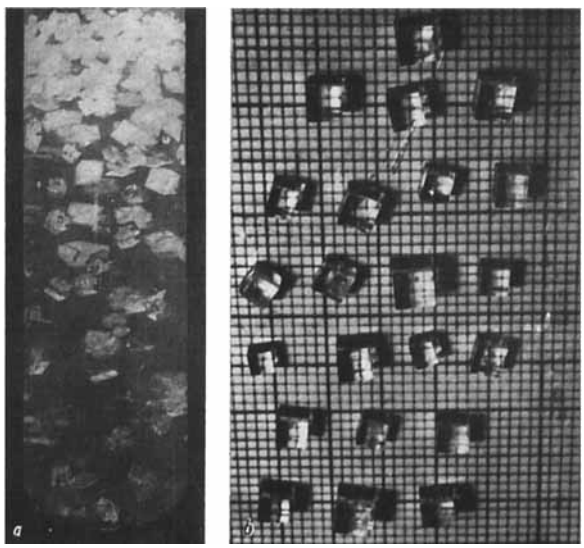

Fig. 2. a) NaCl single crystals growing in silica gel; b) Some of the typical crystals grown in silica gel

2.4. Characterization

Chemical analysis of the crystals inidicated the presence of sodium and chlorine ions. X-ray rotation photographs (Figure 3) were obtained and the calculated lattice parameters agreed with the values reported in the literature. The average density of the crystals measured pyknometrically, was found to be 2.165 g/cm^3. The microhardness determined by Vicker's Hardness Indenter was between 10 and 12 VHN. The crystals exhibited perfect cleavages parallel to {100} faces.

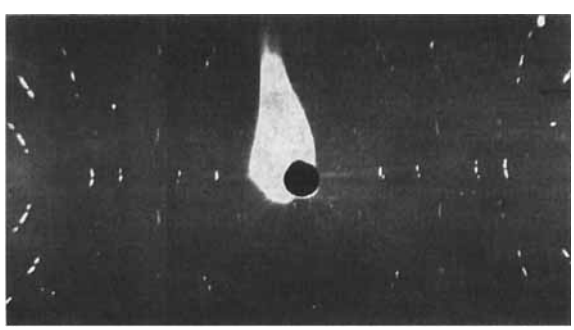

Fig. 3. X-ray rotation photograph of NaCl crystals. Beam direction perpendicular to its axis

2.5. Nucleation and growth

The nucleation density and the growth rate of NaCl crystals was found to depend mainly on the concentration and the amount of HCl acid added above the gel. Solubility of NaCl in HCl acid of various concentrations is shown in Figure 4. From the graphs it is clearly seen that the solubility of NaCl decreases rapidly up to about 5 N HCl and then after it decreases slowly. HCl acid of concentrations less than 5.5 N gave only a few nucleations and the growth rate of the growing crystals was also slow. The rate of growth of crystals was also found to vary with gel density. As the gel density was increased, the growth rate was decreased. In the present study we obtained the best crystals from agar gel when the concentration of HCl acid was 4 N and 7.5 gm of agar agar per liter of saturated solution were used as gel mixture. Good transparent single crystals were obtained from silica gel of density 1.04 g/cc and 6 N HCl acid solution.

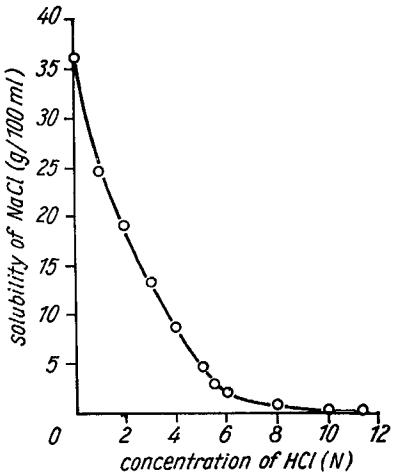

Fig. 4. Solubility curve of NaCl in HCl acid solution (at 25 °C)

2.6. Morphology

In both agar and silica gels, most of the crystals were grown in perfect cubic form. In the fast growth rate (when concentrated HCl was used) hopper and dendritic crystals were found to grow in silica gel. In ionic crystals there is a tendency for atoms to have a strong attraction to the corners and edges of the crystals owing to the large non-directional character of the bonds. If such crystals can grow rapidly then the growth rate at the corners and edges out strips the rate of growth at the centres of the faces and either dendritic or hopper crystals result (MULLIN). In agar gels, other habits of cubic system such as acicular, columnar, and tabular were also obtained near the gel-acid interface region which is due to high supersaturation of NaCl. The same results were also observed in the gel which was prepared with supersaturated NaCl solution. This suggests that habit modifications are occurring only due to the fast growth rate. Figure 5a illustrates the different habits such as equant, bladed, tabular and acicular. The development of different habits is schematically shown in Figure 5b.

2.7. Growth veils

NaCl crystals grown in agar gel exhibits (Figure 6) growth veils near their geometrical centre. These veils were formed during the initial stages of growth and this was more

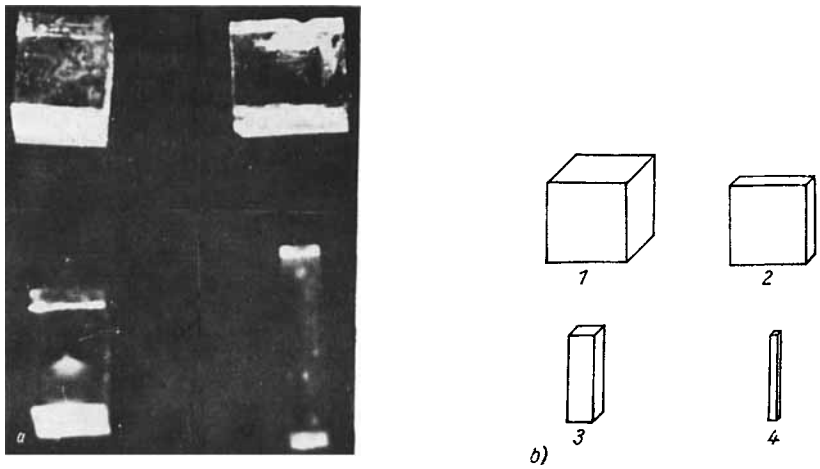

Fig. 5a) Crystals of different habits grown in agar gel; b) Schematic representation of the different habits of the grown crystals: 1 – equant, 2 – bladed, 3 – tabular and 4 – acicular

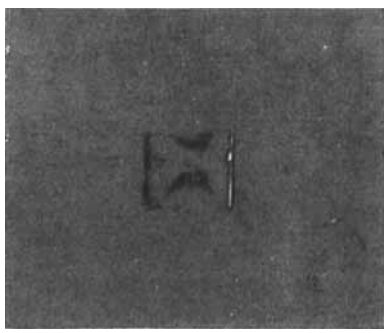

Fig. 6. Growth veil at the centre of the grown crystal

predominent as the concentration of HCl acid was increased. This suggests that growth veils were found due to the rapid growth as reported by HENISCH; EGLI, JOHNSON.

2.8. Etching

Perfection studies of the gel grown NaCl crystals were studied by chemical etching technique. The mixtures of glacial acetic acid and methyl alcohol in the ratio 2:1 was used as the etchant. This etchant produces well defined square-shaped etch pits at the emergent sites of dislocations on the cleaved faces. The average dislocation density was found to be 10^3 cm^{-2}. It has been observed that the perfection of the crystal increases as the rate of growth decreases and also as the distance increases from the diffusion interface. At the bottom of the test tube the rate of growth was very slow resulting better crystals.

3. Conclusions

1. Single crystals of sodium chloride upto 4 × 4 × 4 mm have been grown in agar and silica gels.
2. Crystals with different habits have been obtained in agar gels.
3. Etching experiments reveal the sites of dislocations and the crystalline perfection.

The authors thank Professor A. R. Patel and Professor M. S. Joshi for their keen interest in the work. One of us (JLR) thanks UGC, New Delhi for the award of a Teacher Fellowship, during the tenure of which the present work was carried out.

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(Received January 22, 1980)

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Growth and Characterization of SSD InP Crystals