The Growth of Single Crystals by Controlled Diffusion in Silica Gel

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Monocrystals of calcium tartrate tetrahydrate, neodymium-doped calcium tartrate tetrahydrate, and cuprous chloride have been grown by controlled diffusion in silica gel using both metathetical and decomplexation reactions. Conditions for the optimum growth of the crystals are given and it is shown how the *p*H of the gel, the temperature of its formation, the concentration of the reactants which make up the gel, and the concentration of the reactants which result in the crystal are important in attaining good single crystal products. Crystals have been grown up to 11 mm. on edge in three to four weeks, and in many cases take on a form which, to all outward appearances, seem to have been cut and polished.

In many of today's applications of electronically active materials, it is becoming increasingly important to have these materials with controlled crystallinity or structural perfection. This is true both in industry and in research. The most notable example of the former is the semiconductor industry where the preparation of single-crystals of controlled physical and chemical perfection is a prerequisite to reliable device fabrication. In basic investigations of many of the fundamental properties of solids, monocrystals are required for meaningful results.

Of the various techniques that exist for the growth of single crystals from the melt, or solution, those that require elevated temperatures have inherent difficulties because at higher temperatures (a) crystalline imperfections are more apt to occur due to the disruption of the lattice from thermal vibrations, (b) the danger of contamination from impurities is higher due to their increased solubility with temperature, and (c) point imperfections and lattice strains are generally introduced into the crystal during cooling to room temperature.

Of the growth methods that are available for room temperature crystallization, one that is useful for obtaining substances which have slight solubilities in water, or low dissociation temperatures, or both, and which cannot be satisfactorily grown from the melt or vapor, is crystal growth in gels. The gel provides a three-dimensional network which permits reagents to diffuse, prevents turbulence, remains chemically inert, yields mechanically to the growing crystal, and thus avoids gross constraining forces which are more likely to arise in a crucible or container. The major effect of the gel is to slow down the speed of the chemical reactants so that they can react at a much reduced rate. As a result, crystals can grow much larger than if they were formed rapidly by a similar reaction in water. Furthermore, the crystal growth may be regulated by a molecular mechanism of a nature similar to the passage of molecules or ions through a zeolite. In fact, an ion-exchange type of reaction such as that exhibited by molecular sieves may control the release of reactants, thereby making the silica gel more or less a pseudo-active growth medium.

The growth of crystals in porous media is not a new phenomenon. Laboratory investigations of crystal growth in silica gel date back about fifty years when the subject attracted the attention of Lord Rayleigh (*1*). Hatschek (*2*) did much important work in this field as a result of the interesting work of Liesegang (*3*) who suggested how banded minerals such as agate may have been formed. Holmes (*4*) reviewed previous work on crystallization in media such as agar and gelatin and described many of his own experiments in silica gel.

More recently, interest has been revived in the method as a result of an article by Stong (*5*) and work by Henisch and co-workers (*6*) on a variety of crystals suitable for solid state experimentation. Today the emphasis is on growing large single crystals, as nearly perfect as possible, for application in the fields of electronics, optics, communications, and data processing.

Two techniques will now be described which result in the synthesis of single-crystals by controlled diffusion in silica gels: (a) a metathetical process and (b) a decomplexation process.

EXPERIMENTAL PROCEDURE

To illustrate the first method, a set of conditions will be established for growing calcium tartrate tetrahydrate (C.T.T.), a material of interest because of its dielectric properties. C.T.T. is grown in silica gel by reacting a calcium chloride solution with a gel made from a sodium metasilicate solution and d-tartaric acid. The gel is prepared by pouring the freshly made solution into a 1 in. × 6 in. glass test tube until it is two thirds full and allowing the solution to set until it becomes semisolid. It is important that the test tube be capped with a saran-covered cork stopper to prevent loss of water. Such a loss dries out the gel and affects subsequent chemical reactions because of changes in the gel structure.

It was observed that after setting, liquid appears on the surface of the gel. This squeezing out phenomenon is called syneresis and is probably due to a contraction of the gel during gelation.

The phenomenon of gelation was marked by several stages. When the sodium metasilicate and tartaric acid were first mixed, the solution was transparent; then an opalescence appeared which increased until after the gel had set. The solution became more viscous with time. Shaking the solution gave evidence of elasticity, and after gelation, distortion of the gel by tipping the test tube caused a deformation of the surface which returned to its original form after the test tube was righted.

The time of gelation was observed to be a function of *p*H of the initial solution, the temperature at which the gel is formed, and the concentrations of the reactants. Solutions of sodium metasilicate and tartaric acid were made up to *p*H's varying from 3.5 to 8 and gelation times were measured. It was found that the time of set was proportional to the hydrogen ion concentration in the range of pH used, with almost immediate gelation occurring near $p\text{H} = 7$ and a period of about three weeks required for $p\text{H} = 3.5$, at room temperature.

The temperature of gelation had a profound influence on the time of setting of the gel. At room temperature, for a given set of concentrations on reactants, gelation took about twenty days. By raising the bath temperature to 40°C., gelation occurred in three days, or the time of set was reduced by a factor of 7.

The concentrations of reactants did not seem to affect the gelation time except that there is a lower limit to the concentration of sodium metasilicate in order to give sufficient strength and rigidity o the gel to set.

It was also observed that the nature of the gel was influenced by the *pH* and thus, by the time of gelation. Gels which formed rapidly, at or near $p\text{H} = 7$, were rigid and very viscous, while at lower pH's the gels were softer and seemed more inclined to yield to growing crystals. With the above considerations in mind, it was decided to form the gel under the following conditions: to a solution of sodium metasilicate whose density was 1.0339, made from 21.6 g. of sodium metasilicate in 250 cc. of water, 1 normal tartaric acid solution was added until the pH was 3.5. The pH of the solution was measured by wetting narrow range *pH* paper (3.4 to 3.8) with the solution and reading the color. The resulting solution was poured into test tubes, which were capped tightly, and the test tubes were immersed in a 40°C. thermostatted water-bath and after three days gelation was complete.

To determine the optimum concentration of calcium chloride for reaction in the gel, solutions with concentrations from 0.01 to 2.0 normal were made. These solutions were carefully pipetted on top of the gel in order not to break the surface and substructure. It was observed that nucleation took place immediately at the gel face, and milky white band, about ¼ to ½ in. thick, of small crystals were formed, the thickness of the band depending on the concentration of the calcium chloride solution. From the bottom of the nucleation band where nuclei occurred, clear single crystals started to grow after several hours, increasing in size until the weight of the larger crystals caused them to detach and fall to the lower parts of the test tube. Figure 1 shows the growing area from one such tube with several completed crystals. The crystals vary in size from 2 × 2 to 6 × 11 mm. It was found that the one normal solution resulted in the largest sized crystals, the largest number of crystals, and the clearest crystals.

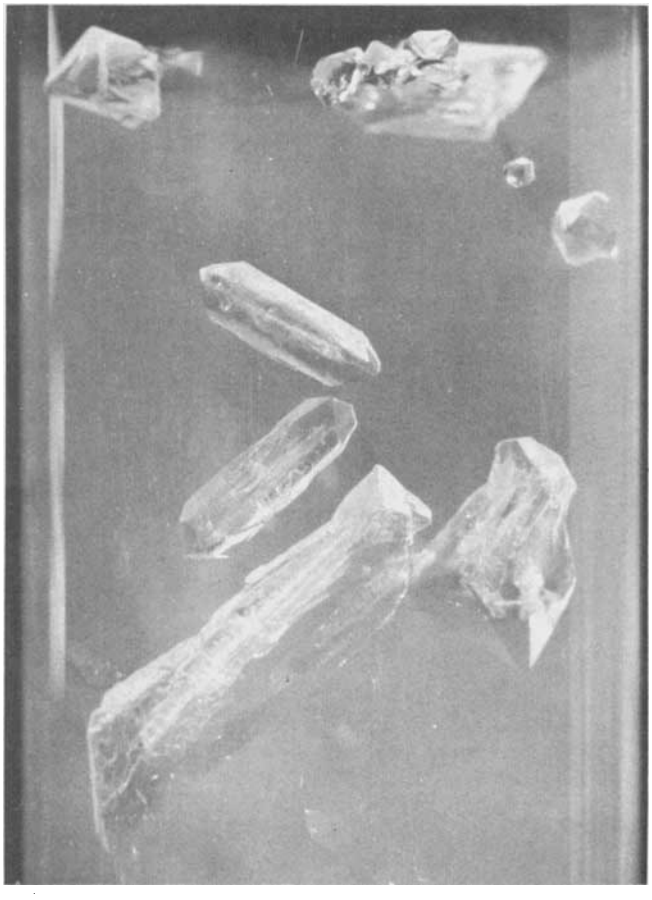

Fig. 1. Single crystal calcium tartrate tetrahydrate.

After several weeks, the gel was carefully removed from the test tube with a spatula, the crystals washed free of gel with water and air dried.

If doped crystals are desired, the nutrient may contain the dopant ion in solution at some convenient concentration. Neodymium doped (0.1 atomic per cent with respect to calcium) calcium tartrate tetrahydrate crystals have been prepared by adding neodymium chloride to a solution of calcium chloride and by supporting the mixed solution on a tartaric acid gel. The resulting crystals were harvested after three weeks when the size appeared to remain constant.

To illustrate the second method, that is the decomplexation process, cuprous chloride (C.C.) single crystals were prepared by the gel method. In this case, it would be difficult to prepare C.C. by a metathetical reaction. However, it is known that C.C. (*7*) forms a soluble complex in a concentrated hydrochloric acid solution. A saturated solution of C.C. in 6N hydrochloric acid was prepared as the nutrient solution and floated on a gel prepared from 1N hydrochloric acid and 0.5 mol. sodium metasilicate titrated to a pH of about 4 and allowed to set at 40°C, (*8*). The complex diffused into the gel and decomplexed as follows:

$$H_xCuCl_{x+1} \rightarrow XHCl + Cu\ Cl$$

Crystals of cuprous chloride appeared as tetrahedra near the gel-nutrient interface.

RESULTS

The calcium tartrate tetrahydrate crystals grown as described above took on a form which to all outward appearances seemed to have been cut and polished. They occurred in two typical habits, one bipyramidal and the other which can be best described as trapezohedral, with a few forms in different stages of development. Many of the crystals were colorless and clear, but some were flawed with veils. Back reflection X-ray laue patterns confirmed their single-crystallinity.

The neodymium-doped calcium tartrate tetrahydrate crystals were tinted light purple, indicating the presence of the neodymium ion. The concentration of the neodymium was determined by emission spectroscopy to be 0.1 ± 0.25 atomic per cent per calcium ion, based on prepared standards.

The tetrahedrally-shaped cuprous chloride crystals were obtained as large as ⅜ in. on edge, were partly skeletal in form, and were not crystal clear.

CONCLUSIONS

The gel method for growing single crystals offers the advantage of a room-temperature growth technique and is particularly suited to the preparation of materials which dissociate, decompose, or react with the container at elevated temperatures. Where the solubility of the material is convenient, it is possible to grow crystals either doped or undoped, by metathetical type reactions. Where this type of reaction is not available, the formation of a suitable complex of the desired material as the nutrient, with its subsequent decomposition in a gel can be used as the growth method.

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Transport of Toluene Through Fully Swollen Polyethylene

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Experiments have been carried out to measure the permeation of tritium-labeled toluene through polyethylene films fully swollen with chlorobenzene, mesitylene, cumene, toluene, ethylbenzene, cyclohexane, tetrahydronaphthalene, and decahydronaphthalene. The results show characteristic Arrhenius temperature dependence over the range 25 to 40°C. The permeation of toluene through the films appears to be enhanced by increased solubility of the swelling agent (estimated from the work of others) in the film and there also appears to be a rough correlation between permeability of toluene and the boiling points and vapor pressures of the swelling agents. The range of permeabilities measured at 25°C. is 2.09 $\times$ 10^{-7} to 0.51 $\times$ 10^{-7} sq.cm./sec., the extremes of measured permeation activation energy, E_p, are 11.41 to 16.68 kcal./mole, and the pre-exponential factor, P_o, falls within the interval 36.59 to 1.29 $\times$ 10^5 sq.cm./sec. A very definite linear relationship or compensation effect is evident between P_o and E_p. Except as mentioned above, none of these quantities appears to correlate uniformly with the following properties of swelling solvent: molecular weight, dipole moment, specific gravity, vapor pressure, boiling point, heat of vaporization, critical temperature, viscosity, surface tension, molar volume, molecular area or other molecular dimensions.

In the many reported studies of transport of gases and vapors through polymers, experimental measurements almost always involve a significant partial pressure or concentration gradient within the material. In such experiments the solute or diffusing species interacts with the polymer, frequently causing swelling, and thereby brings about nonuniform transport properties in the medium along the direction of the concentration gradient. Because of this phenomenon the ordinary form of the diffusion equation,

$$D\nabla^2 C = \frac{\partial C}{\partial t} \tag{1}$$

is inapplicable to such systems. However the more fundamental form of the diffusion equation,

$$\mathrm{div}(D\,\mathrm{grad}C) = \frac{\partial C}{\partial t} \tag{2}$$

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