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NASA TECH BRIEF

Growing Single Crystals in Silica Gel

Modern applications of materials in electronics often require single crystals with controlled purity and structural perfection. Various techniques exist for growing such crystals from a melt or from solution. Of these, the methods which require high temperatures are likely to produce less perfect crystals, due to the higher frequency of dislocations produced by thermal vibration, the increased solubility of impurities, and the greater number of point imperfections caused by thermal stress during cooling.

Results have been published of past research on the technique of growing crystals at room temperature by controlled diffusion through a silica gel medium. Although this technique is not new, the results demonstrate the effect of many variables on the growth of single crystals, and show the possibility of using the gel technique to grow single crystals of some materials potentially useful in electronics.

The first results describe the effects of various parameters on the formation of silica gel from a tartaric acid solution of sodium metasilicate. In the pH range from 3.5 to 8.0, the time required for the gel to set is proportional to the hydrogen ion concentration. At room temperature, gelation occurs almost immediately at a pH of 7 or more; at a pH of 3.5, it takes about three weeks.

The time required for gelation is also strongly dependent on the temperature. When the pH 3.5 solution is incubated at a temperature of 40°C, the gelation time is reduced to three days.

Most important, however, is the observation that the nature of the gel itself depends upon pH. Gels formed at low acidity tend to be rigid and very viscous, while those formed from more acid solutions are softer and more yielding. In order to minimize the resistance of the medium to growing crystals, the more acid solutions are recommended.

Two types of chemical reaction have been investigated. The first is a metathetical (the ions of two soluble compounds exchange partners to produce at least one insoluble product) reaction used to produce calcium tartrate tetrahydrate crystals, of interest because of their dielectric properties.

To grow these crystals, a solution of 21.6 grams of sodium metasilicate in 250 cc of water is titrated with 1 normal tartaric acid until the pH of the mixture reaches 3.5. The resulting solution is poured into 1 × 6-in. test tubes, filling each of them two-thirds full. The test tubes are then tightly sealed and incubated for three days at 40°C, until gelation is complete. A nutrient solution of calcium chloride is then suspended on top of the gel. After several hours crystal growth begins downward from the gel face and continues for several weeks until the reagents are exhausted. It has been found experimentally that a 1N solution of calcium chloride produces the greatest number of the largest (up to 6 × 11 mm) and clearest crystals.

If doped crystals are desired, the nutrient solution may contain the dopant in any desired concentration. Neodymium doped calcium tartrate tetrahydrate crystals have been prepared by adding neodymium chloride to the solution of calcium chloride that is supported on top of the gel. The light purple color of the product confirms the incorporation of neodymium into the growing crystals.

The second reaction studied is a decomplexation reaction (a normally insoluble compound is dissolved by formation of a complex, and the crystal is grown through the reverse reaction) used to produce cuprous chloride crystals.

(continued overleaf)

In this case, the gel is prepared at a pH of 4 using hydrochloric acid, and the nutrient, a saturated solution of cuprous chloride in 6N HCl, is suspended on top of the gel. The complex (H_xCuCl_{x+i}) diffuses into the gel, dissociates, and crystals of cuprous chloride (CuCl), tetrahedra up to 9 mm on edge, are grown near the gel-nutrient interface.

Notes:

1. The gel technique may be used to grow single crystals of many materials which decompose, dissociate, or react with the container material at high temperatures. It may be used to produce single crystals of other materials where stoichiometric effects are important.
2. This technique may be of interest to persons involved in growing, determining the properties, and using single crystals. Potential applications of crystals grown by controlled diffusion through silica gel are in the area of optical modulators and infrared window materials.
3. A report on this project has been published in the AIChE Journal, Vol.15 No. 2 (March 1969) pp. 206-209.
4. No further documentation is available. Specific questions, however, may be directed to:

   Technology Utilization Officer
   Headquarters
   National Aeronautics
   and Space Administration
   Washington, D. C. 20546
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Patent status:

No patent action is contemplated by NASA.

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