Growth of Calcite Crystals in Gels

H. J. Nickl and H. K. Henisch[1]

Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania

ABSTRACT

Procedures for the growth and doping of calcite crystals in gel systems are described. Crystals surrounded by gel tend to incorporate the silica network with its structure intact. Hybrid methods avoid this contamination. Crystals then grow in small volumes of solution, the solution being replenished by diffusion through gel filtering media. The solution cavities can be seeded with calcite crystals which then serve as substrates for epitaxial growth. Weight increases by factors up to 10 are easily achieved.

Calcite crystals have well-known applications in optical instrumentation and laser technology (1), and since the sources of natural specimens appear to be diminishing, a special interest attaches to all methods of growing the material artificially. Control over the nature and concentration of dopants should be achieved at the same time. Previous growth attempts of calcium carbonate by a hydrothermal method have been described by Ikornikova and co-workers (2), experiments on growth in solution by Gruzensky (3) and by Kaspar (4), and in electrochemical systems by Barta and Zemlicka (5). Morse and Donnay (6) and McCauley (7) have dealt with growth in gels, the last with emphasis on reaction mechanism and phase aspects. In the present paper some new procedures for gel growth are described and the factors which control crystal perfection are discussed, with special reference to the inclusion of silica. Experiments with rare earth and transition metal dopants are also reported.

Growth Methods

The formation of calcite is accomplished by the reaction between carbonates and calcium salts in sodium metasilicate gels. Two methods have been developed for this purpose. In the first the gel itself contains the carbonate. An aqueous mixture of sodium metasilicate and a carbonate is prepared and the *p*H adjusted to between 7 and 8, usually by means of acetic acid. After the gel has set, calcium salt solution is put on top and allowed to diffuse. Test tubes (25 x 200 mm) are used in the ordinary way (Fig. 1), but bottles up to ½ gallon volume were employed for some of the large scale experiments. Attempts to mix the calcium salt with the gel in the same way fail because calcium silicate precipitates at and above a *p*H of 7. At lower *p*H values this precipitation is avoided, but any subsequent diffusion of carbonate leads to CO_2 production which destroys the gel.

In the second method the neutral gel is initially free of calcium and carbonate ions. The reagents diffuse into it from two sides and form calcite where they meet. This is conveniently done in U-tubes (25 x 200 mm) or in tubes (45 x 130 mm) with fritted inserts (Fig. 2).

There appears to be no significant difference between the merits of the two methods; both produce well-shaped calcite rhombohedra of up to 6 mm size, within 6 to 10 weeks. A few spherulites of aragonite and vaterite also appear. The three modifications have been verified by comparison of the d-values derived from x-ray diffraction measurements with those compiled by Swanson and Fuyat (8, 9) and by McConnel (10). Room temperature (25°C) proved to be optimum for growth. High temperatures, *e.g.*, 70°C or so, favor the formation of aragonite (11-13) and cause bubbles to appear which disrupt the medium.

In all cases the gels were made from analytic grade $Na_2SiO_3 \cdot 9H_2O$, with final densities between 1.02 and 1.03, corresponding to between 0.17 and 0.23M Na_2SiO_3 in the gelling solutions. As a source of carbonate ions, solutions of Na_2CO_3 (*p*H 11.6), $(NH_4)_2CO_3$ (*p*H 9), $NaHCO_3$ (*p*H 8.6), and NH_4HCO_3 (*p*H 8.4) were used, and the calcium was derived from $CaCl_2$ or $CaAc_2$. The combination which yielded the best results was found to be $(NH_4)_2CO_3 + CaCl_2$ in equal concentrations (0.16M). Na_2CO_3 is less suitable on account of its high *p*H which, on neutralization, leads to high sodium acetate concentrations. These have been found to affect the quality of the resulting crystals adversely whereas ammonium acetate appears to have no such effect.

Growth Products

Crystals grown in the normal way as described, although well-formed rhombohedra (Fig. 3), are almost invariably turbid, obviously due to inclusions. As far as metals are concerned, the crystals contain

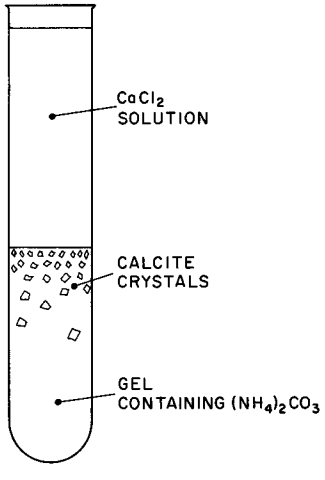

Fig. 1. Test-tube method for growing calcite crystals in gel

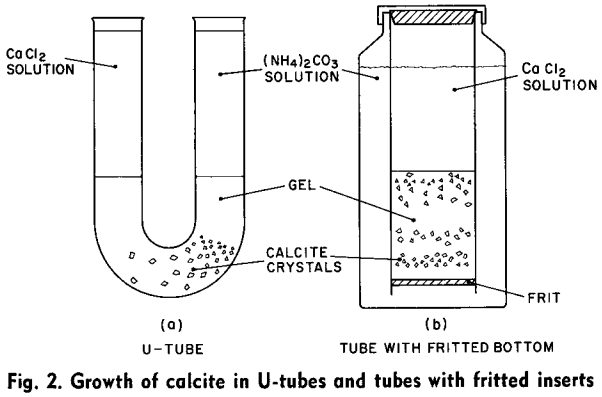

Fig. 2. Growth of calcite in U-tubes and tubes with fritted inserts

[1] Also Department of Physics.

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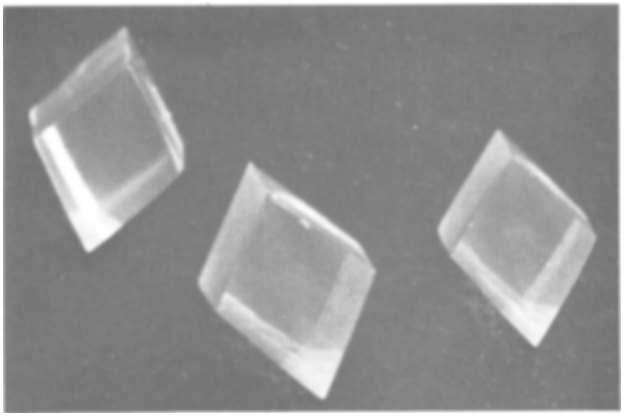

Fig. 3. Rhombohedra of gel-grown calcite. Edge lengths: 2.5 mm

about 80 ppm of Sr and smaller amounts of Ba, Mg, and Cu, as determined by emission spectroscopy. However, they also contain relatively large amounts of Na and Si (as SiO_2), both nonuniformly distributed, but not in coinciding patterns, as shown by electron microprobe tests. Quantitative analysis showed that the amount of SiO_2 varies between 0.47 and 1.7% when prepared in gels of varying density between 1.02 and 1.03 g/cc. Despite this gross contamination, the specimens have well-developed and smooth crystal faces. Dissolution of a turbid crystal in acid leaves a residue which maintains the shape of the original specimen. Figure 4 shows this after partial solution; the dense inner core is part of the original calcite crystal. The surrounding residue turns out to be silica gel which can be examined by the freeze-drying technique already described (14) and shown to have the same structure as the original growth medium (Fig. 5). It is clear from the results that the silica network which constitutes the gel is incorporated into the growing crystals more or less intact. In this way, calcite differs greatly from other gel-grown crystals, *e.g.*, calcium tartrate, which are surprisingly free from silica contamination. In these cases, the gel is bodily displaced by the advancing growth surface, whereas calcite permeates the silica network while maintaining a high level of short-range order. In this respect, the gel-grown specimens resemble certain natural calcite structures, *e.g.*, the spikes of sea urchins.

A few of the crystals are found to grow in fissures, and thus at the boundaries between gel and solution. These are turbid to the extent to which they overlap the gel and clear to the extent to which they grow in solution. The two regions can be clearly seen in Fig. 6. The same observations were made on crystals

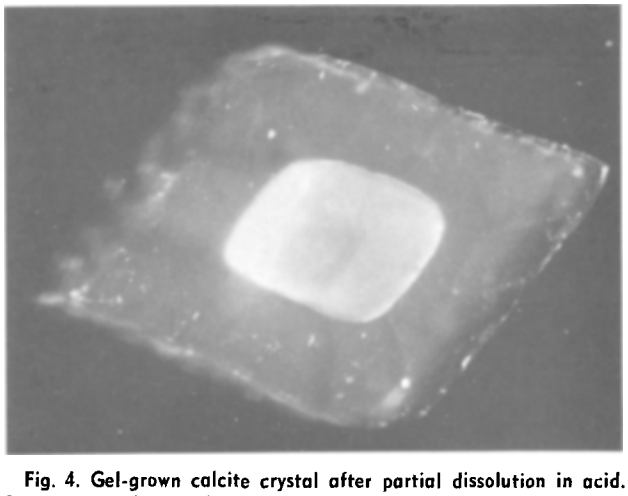

Fig. 4. Gel-grown calcite crystal after partial dissolution in acid. Original edge length: 2.5 mm.

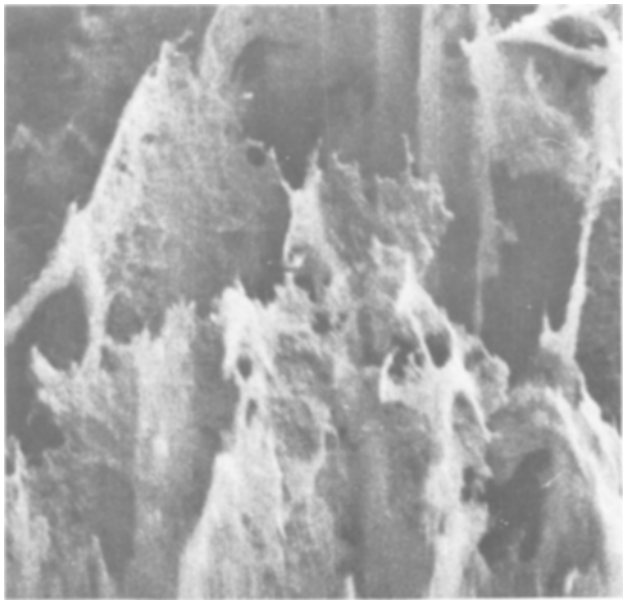

Fig. 5. Gel structures revealed by an electron scanning microscope after vacuum freeze drying: (a) gel residue after crystal dissolution.

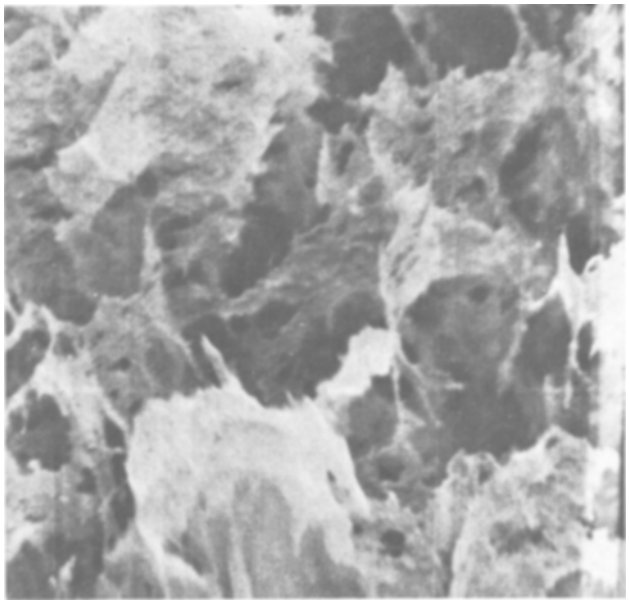

Fig. 5 (b). Normal growth medium. x3000

of aragonite and vaterite grown by the same procedures.

Doping

The methods described above can also be used for the preparation of doped crystals. Dopants in the form of chlorides or nitrates can be incorporated in the sodium metasilicate solution before gelling or else in the supernatant solution. Small amounts did not affect the growth habit of the calcite crystals, but high dopant concentrations were found to prevent the growth of regular rhombohedra. The maximum permissible concentrations for regular growth differed for the various metal ions examined. For Co^{+2}, Ni^{+2}, Cu^{+2}, Mn^{+2}, Mg^{+2}, and Zn^{+2}, they were of the order of 10^{-3}M in the gel and 5 to 20 times higher in the supernatant solution. For Cr^{+3} the maximum is about 0.1M (in the gel). All these metals form hydroxides which are insoluble in pure water but somewhat soluble in the presence of NH_4OH and ammonium salts. For Nd^{+3}, Ho^{+3}, Er^{+3} and Fe^{+3}, the maximum permissible concentrations in the gel were of the order

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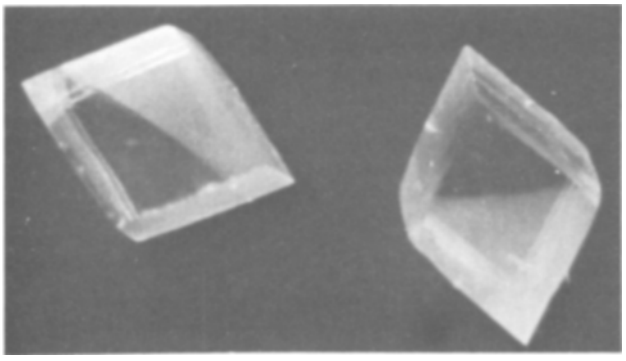

Fig. 6. Boundaries between calcite regions grown in gel and those grown in solution. Edge lengths: 2.5 mm.

of 10^{-4}M or, as in the last case, too small to be readily determined. These metals form hydroxides and carbonates which are even more insoluble than those listed above under the growth conditions employed. It is therefore reasonable to assume that they precipitate earlier in microcrystalline form. Subsequent calcium carbonate growth would then occur by epitaxy, as suggested by Johnston and co-workers (12, 15), and discussed by McCauley (7) who list many other references. Epitaxy would lead to growth without any particular relation to the rhombohedra found at lower concentrations. For the metals which form more soluble hydroxides and carbonates, the same effect would occur at higher concentrations. This interpretation is in harmony with the fact that dopant concentrations which are high enough to destroy regular growth also lead to greatly increased nucleation. Valency consideration must, of course, enter into this picture, but the high permissible concentrations of Cr^{+3} discount their dominating importance. For reasons which are not yet clear, there is an enrichment of dopants in the crystals by a factor of about 100, as compared with the average dopant concentrations in the gel.

It was shown by means of the electron-microprobe that the dopants are uniformly distributed within the crystals, whether clouded by silica networks or not. Of the crystals doped with the above elements, only those containing Mn were found to be (slightly) photoluminescent in the orange region of the spectrum, and also cathodoluminescent in the red.

Hybrid Procedures

The success of the gel method is believed to depend, in the ordinary way, on two principal features: (*a*) crystals are grown by diffusion, which means that the solute concentration at the growth boundary is self-regulating in accordance with the needs of the growth process itself, and (*b*) nucleation is suppressed by the gel, partly because it acts as an efficient filtering medium and serves also to isolate a good deal of solute in cavities which are too small to permit homogeneous nucleation to be effective. As shown above, the method has, at any rate for calcite, the disadvantage of leading to substantial inclusions of silicate gel network into the growing crystals. This suggested that hybrid methods should be more successful. In these, crystals are grown in solution without, in principle, losing the general benefits of the gel method. To achieve this, the volume of the solution should always be comparable with that of the growing crystals, a condition not easily achieved, and especially not during the initial stages of growth. In practice, a compromise must therefore be made, the solution volume being kept as small as is technically feasible. The solute must be replenished by diffusion in order to approach the self-regulating boundary concentration mentioned above, and the diffusion medium must be a gel. These requirements distinguish the optimum arrangement

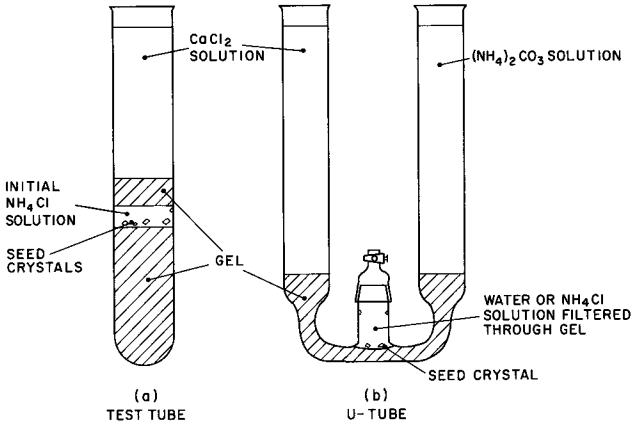

Fig. 7. Systems for calcite growth by hybrid gel method

from the systems, otherwise similar, proposed by Torgesen and Peiser (16). Figure 7 gives two examples. In the test-tube system on the left, sodium metasilicate solution is floated on a concentrated solution of NH_4Cl and allowed to gel before adding the supernatant $CaCl_2$ solution. Crystals then grow primarily in the solution belt. Unwanted nucleation on the wall of the tube can be diminished by giving it an initial gel coating. The system on the right involves diffusion of the reagents through separate gel columns, and the entire growth medium is filtered in this way. The solution can be seeded with a small calcite crystallite derived from a pure gel system or from other sources. Epitaxial growth occurs, and the new layers are clear, no matter whether the seed contains a silica network or not. When clear seeds are used, no boundary between substrate and new growth can be optically detected. Weight increases by factors up to 10 are easily achieved.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1970 JOURNAL.

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