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Growth of strontium tartrate tetrahydrate single crystals in silica gels

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Growth of single crystals of strontium tartrate tetrahydrate by controlled diffusion in silica gels has been narrated. In the field of material science, there is always a keen and competitive race to grow perfect single crystals with sufficient purity and perfection. Successful attempts to larger as well as more perfect crystals of SrTr are described in this paper and thus probably the largest (about 2 in. across) ever grown size of gel-grown products is reported here. The effect of several parameters, e.g. crystallization apparatus, environmental temperature, reactant concentration, gel density, gel-ageing and gel pH, on the size, quality and morphology of the crystals has also been studied.

1. Introduction

Increasing use is being made of chemical reactions in the preparation of solid-state materials. Two or more species react together to form a desired solid product along with one or more water-soluble or gaseous products. Amongst such reaction techniques [1–6], one important technique [2], growing crystals in a gel, has been investigated by several laboratories [2, 7–9].

It appears that little effort has been expended on the growth of SrTr single crystals. Henisch *et al.* [2] were successful in growing SrTr single crystals using the gel method, but paid little attention to the size and purity attainable. The present study was aimed at growing large, transparent single crystals of SrTr.

2. Crystal procedure

The gel was prepared from a "pure" sodium silicate [10] solution of specific gravity 1.04 by acedification with either acetic or tartaric acid. The change in pH with addition of acid to 60 ml sodium silicate solution is shown in Fig. 1A and B. In our experiements the best results were obtained at a pH between 6 and 9. Following the beaker-system of growth of Henisch *et al.* [2], of pH 6.5 set with tartaric acid, and a few ml 1 N $SrCl_2$ solution was placed upon it. Surface nucleation was discerned within 3 to 4 days. The tiny crystals were removed from the surface mechanically and, after carefully washing the surface of the gel with double-distilled water, without disturbing the set gel, the beaker was filled to the brim with 1 N $SrCl_2$. This procedure yielded good single crystals up to 1 in. across.

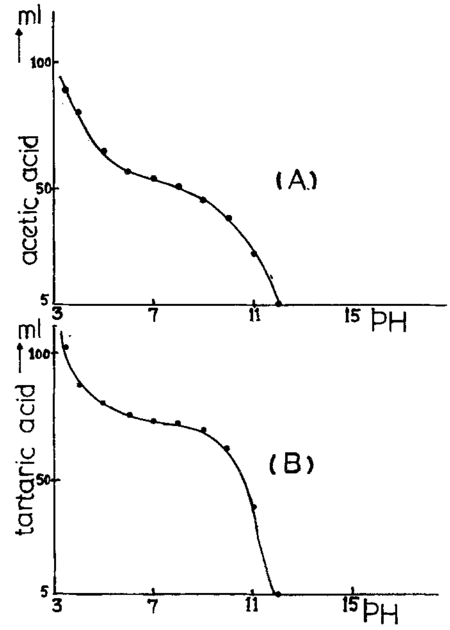

Figure 1 Variation of gel pH by addition of (A) acetic acid and (B) tartaric acid to 60 ml aqueous "pure" sodium silicate solution.

In the second method, employing the single tube system [10,11], gel of pH 6.5, acedified with CH_3COOH was placed in the crystallization beaker covered with 1 N $SrCl_2$ solution, 1 N sodium tartrate solution was poured into a 2 cm diameter tube, open at both ends. This method produced crystals of up to 1 in. across. Although the smaller crystals were well-faceted and highly transparent, the larger ones looked less perfect. In both methods, crystallization was complete within 3 to 4 weeks. The chemical reaction responsible for crystal growth is as follows:

$$SrCl_2 + Na_2C_4H_4O_6 \rightarrow SrC_4H_4O_6 \downarrow + 2\,NaCl. \quad (1)$$

The unwanted reaction product, i.e. NaCl was occasionally pipetted off when using the double tube system [10, 11].

3. Observations and discussion

3.1. Nucleation control

In attempts to grow still larger and more perfect crystals, small amounts of several reagents such as NH_4Cl, NaCl, KCl, LiCl were incorporated in the gel itself before setting, and it was observed that the addition of NH_4Cl produced encouraging results. With the addition of 5 ml aqueous 1 N NH_4Cl solution to 100 ml pre-set gel, only a limited number of nucleation sites developed which resulted in the growth of prismatic crystals up to 2 in. long. A 250 ml beaker in which only two large crystals have grown is displayed in Fig. 2.

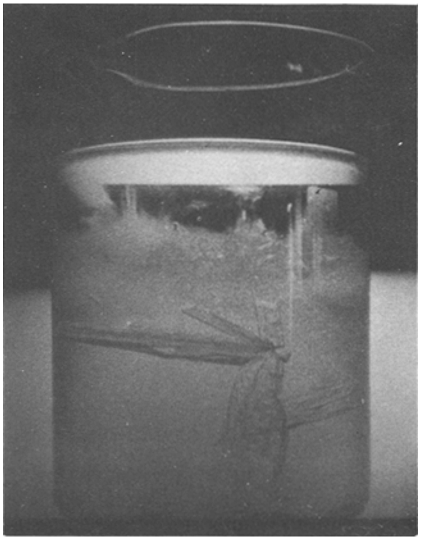

Figure 2 The crystallization beaker (250 ml capacity) showing controlled nucleation: the large crystals are seen to have sprouted from the growth nuclei.

The density of nucleation centres plays a vital role in the crystal size attainable, which governs the merit of the process of growth. The incorporation of a small amount of 1 N NH_4Cl aqueous solution helped nucleation to occur at a few sites only which resulted in the growth of large crystals. This may be due to the increased solubility of SrTr in water containing NH_4Cl. This is supported by the fact that NH_4Cl solution is a good etchant for these crystals. The responsibility of the NH_4Cl in the gel for the growth of large crystals was demonstrated by growing SrTr crystals, employing the reaction,

$$SrCl_2 + (NH_4)_2C_4H_4O_6 \rightarrow SrC_4H_4O_6 \downarrow 2\,NH_4Cl \quad (2)$$

in a single tube system. For the purpose, 0.4 N aqueous solutions of both reactants were used. This reaction produced crystals more than 1 in. long, whereas, reaction 1 never produced crystals of this size. In view of these facts, the double tube system [10, 11] is not preferable. A few single crystals of SrTr grown are shown in Fig. 3.

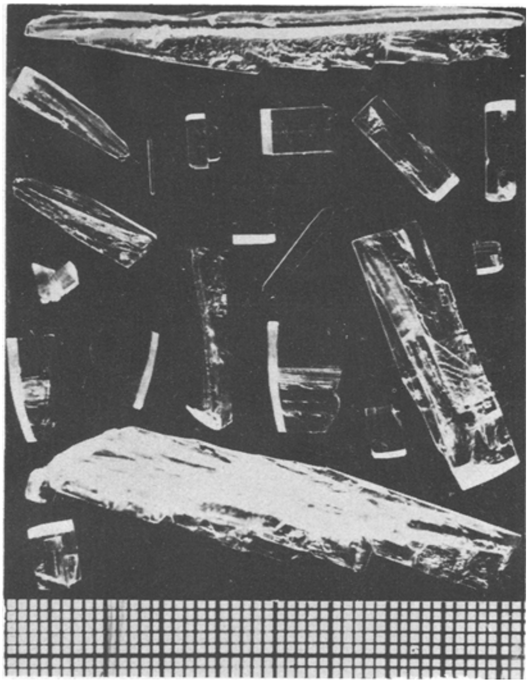

Figure 3 A few gel-grown crystals of strontium tartrate tetrahydrate (mm scale).

3.2. Characterization

SrTr crystals show four molecules of water of crystallization. Many specimens are absolutely clear on visual inspection and show few inclusions. When heated, they become white and opaque.

Rapid and excessive heating causes fracture along the cleavage plane. The pycnometer density is 1.996 g ml^{-1} whilst that computed from cell dimensions [12] is 2.079 g ml^{-1}. The Vicker's microhardness of the crystals is 1.98 Mohs at 10 g load applied for 20 s.

3.3. Crystal morphology

While working with gel solutions of pH between 5 and 7, rhombic prisms bounded by well-developed {0 0 1} and {1 1 0} faces were produced. This habit is shown schematically in Fig. 4A. It is noteworthy that when 1.5 N $SrCl_2$ was used the resulting crystals were simply elongated along [0 0 1] axis which increased the separation of (0 0 1) and (0 0 $\bar{1}$) planes. When 2 N or higher concentrations of $SrCl_2$ were used, the crystals acquired dendritic morphology, the stem of the dendrites being along the *c*-axis.

When the gel solution was above pH 7.5, the brachydome and macropinacoid habit whose faces are parallel to the brachyaxis, *a*, as evident in Fig. 4B, was also observed to have developed in addition to the prism and basal pinacoid morphology of Fig. 4A. It was also noticed that 2 to 3 weeks after the commencement of growth new crystals endowed with a different habit grew in the beaker. These crystals displayed the typical orthorhombic macrodome and brachypinacoid habit bounded by {1 0 1} and {0 1 0} faces that are parallel to the macro-axis, *b*, as shown in Fig. 4C. Growth experiments were also carried out using old gels. Gels aged more than 450 h yielded crystals of the habit of Fig. 4C. It is likely, therefore, that gel ageing tends to increase the growth rate along the *b*-axis, which accounts for the observed change in growth morphology of $SrTr.4H_2O$ crystals.

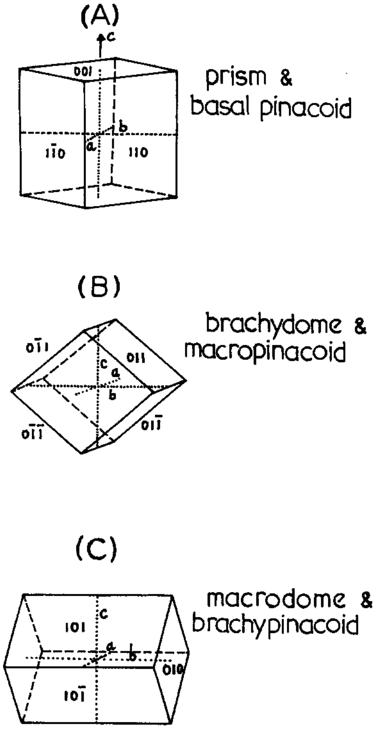

Figure 4 Schematic illustration of the habits of the crystals grown: (A) rhombic prism and basal pinacoid; (B) brachydome and macropinacoid; (C) macrodome and brachypinacoid.

3.4. Effect of temperature

The above experiments were conducted at room temperature (28 to 34° C). To investigate any effect of temperature on the growth behaviour of these crystals, a few experiments were performed between 38 and 43° C. It was observed that using a gel solution of pH 6.5, the crystals with a prismatic habit (Fig. 4A) became far more elongated along the *c*-axis than along other axes, which resulted in long needle-like crystals grown along ⟨0 0 1⟩. These needles were mostly broken while harvesting from the gel network. The growth kinetics of these needles were studied in fresh as well as old gels. Using gels aged for 94 and 196 h the rate of growth of the needles at 39 to 40° C followed a parabolic course, as shown by curves I and II, respectively, in Fig. 5A. The parabolic

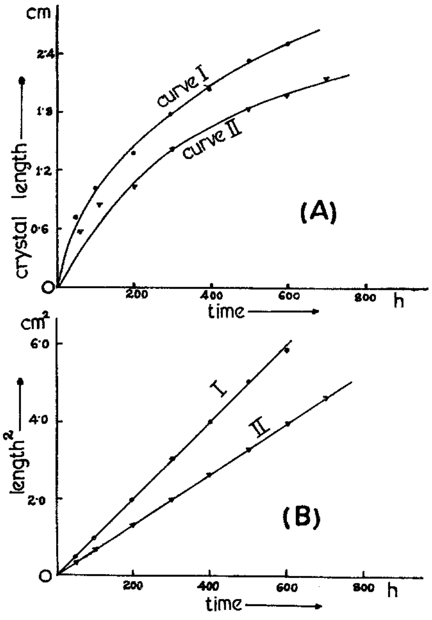

Figure 5 Growth kinetics of crystalline needles in a gel 94 h old (curve I) and 196 h old (curve II). (A) Needle length versus time; (B) Squares of needle length versus time.

kinetics are characteristic of a one-dimensional-diffusion-controlled process of growth, represented by the equation [13],

$$R = [Dt]^{1/2}$$

A plot of the square of needle length against time gave straight lines as shown in Fig. 5B. This is in agreement with the kinetic study of ionic crystals [14, 15].

The growth rate constants, D, determined from these curves, are shown in Table I. It is evident that an older gel would adversely affect the diffusion of ions, which probably does not help larger needles to grow. This is in agreement with the views of Liaw and Faust [15].

TABLE I

Age of gel (h)	Growth-rate constant, D ($\text{cm}^2\ \text{h}^{-1}$)
94h	0.011
196h	0.005

3.5. Crystal habit faces

The finished faces of all crystals grown between 25 and 32° C showed rectangular etch pits with different distributions, being more crowded near the edge. The surfaces of crystals grown between 33 and 43° C also showed well-developed growth layers, varying in thickness between 10^{-2} and 10^{-4} cm, with sharply delineated edges as determined by multiple beam interferometry [16]. A typical (1 1 0) face exhibiting growth layers, originating from the edges, along with the few rectangular pits is shown in Fig. 6. The average dislocation density, computed by the etch-pit count method, was found to be 10^1 to 10^2 cm^{-2}. No etch pit rows resembling tilt-twist boundaries were observed. These facts indicate that the crystals grown are of a high perfection.

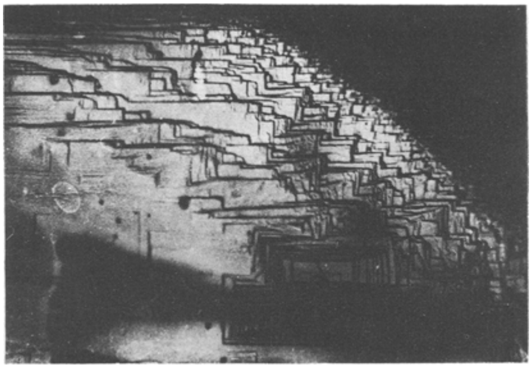

Figure 6 A typical (1 1 0) as-grown face of SrTr crystals × 90.

4. Conclusions

(1) Good single crystals of strontium tartrate tetrahydrate up to about 2 in. across, the largest yet grown by the gel method, have been obtained.

(2) The nucleation characteristics depend largely on the manner in which the gel is prepared for crystal growth.

(3) Basal pinacoids and macropinacoids grow at low and high pH respectively.

(4) Higher temperatures (about 42° C) favour the growth of needle-like crystals.

(5) Crystal growth in gels is a one-dimensional diffusion controlled process.

(6) Gel ageing tends to impede the growth rate.

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