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Growth of $Ca_x Sr_{1-x} C_4H_4O_6 \cdot 4H_2O$ mixed crystals and their characterization

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The growth of mixed crystals of $Ca_xSr_{1-x}C_4H_4O_6 \cdot 4H_2O$ in a gel medium, and their characterization by suitable physical and chemical methods, are reported. Silica gel, obtained from sodium metasilicate solution with a strongly acidic cation exchanger in the H-form, was used for crystal growth. The calcium, strontium and iron contents in the crystals, the lattice parameter along *b*-axis and the density are determined and compared with the data reported in the literature. The micromorphology of the as-grown and etched surfaces is also briefly described.

1. Introduction

Compounds of tartaric acid find various practical applications in science and technology [1]. Among these compounds, tartrates of calcium and strontium crystallize in the orthorombic system with space group $P2_12_12_1$ having four molecules in the elementary unit cell [2, 3]. Although their electrical and optical properties are yet to be investigated, the growth of single crystals of tartrates of calcium and strontium and their solid solutions of various compositions has recently drawn considerable interest [4–9]. Since these compounds are sparingly soluble [6, 8] and decompose at fairly low temperatures [9], successful growth of pure and mixed crystals has been reported in silica gel [4, 5, 7, 8]. However, during growth, the silica gel prepared from commercial sodium metasilicate and tartaric acid (H_2Tr), according to the reaction

$$Na_2SiO_3 + H_2Tr + H_2O \rightarrow H_4SiO_4 + Na_2Tr. \qquad (1)$$

was employed. The gel thus obtained is always contaminated with sodium tartrate and other impurities inherently present in the initial reactants. Consequently, the optical quality of the gel-grown crystal is expected to be poor. The quality of the crystals can be improved by using a cross-linked polymeric acid (RSO_3H) instead of tartaric acid for the hydrolysis reaction [10]:

$$Na_2SiO_3 + 2RSO_3H + H_2O \rightarrow 2RSO_3Na + H_4SiO_4. \qquad (2)$$

In this case, except for the Na^+ ions, other metal ions (Me^+) are removed simultaneously according to reaction

$$Me^+ + RSO_3H \rightarrow RSO_4Me + H^+. \qquad (3)$$

Patel and Arora grew single crystals of tartrates of strontium [5] and mixed calcium–strontium tartrates [7, 8] in single beaker and single-tube-beaker systems. Even in the same system the growth of needles in addition to crystals with definite habits was observed. These authors [8, 9] used needles grown just below the gel interface for the determination of density and lattice parameter along the *b*-axis, and crystals of brachydome habit for the estimation of dislocation density.

In the present work the growth of mixed crystals of Ca and Sr tartrates in silica gel using the three-layer single tube and the U-tube systems, and their characterization by suitable physical, chemical and X-ray methods, are reported. The results are briefly compared with those reported by Patel and Arora [7–9].

2. Experimental procedure

Crystal growth was accomplished in single-tube (single-diffusion) and U-tube (double-diffusion) systems. In the case of single-tubes, the usual double-layer and three-layer systems were used. The former consisted of the layer of gel prepared according to Equation 1 and a further layer of

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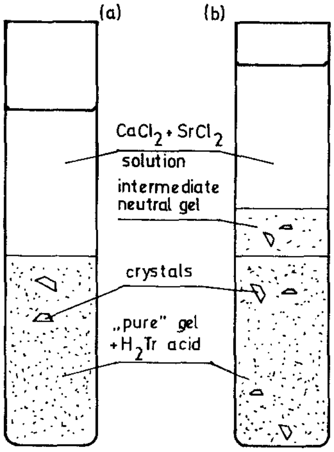

Figure 1 Single-tube systems of crystal growth: (a) two-layer system, (b) three-layer system.

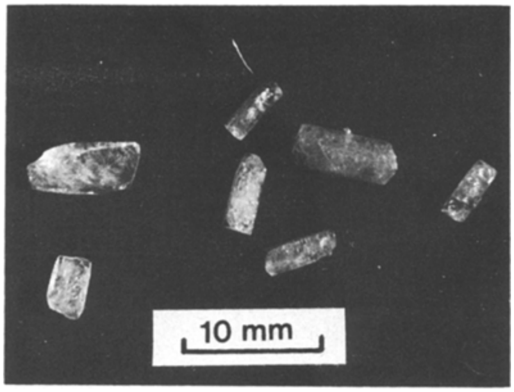

Figure 2 A few gel-grown crystals of strontium–calcium tartrate tetrahydrate.

chloride solution, while the latter contained an additional layer of a neutral gel, prepared according to Equation 2, above the bottom gel layer acidified with H_2Tr (Fig. 1). In the case of U-tube system, solutions of 1M H_2Tr and 0.5M $CaCl_2$ + 0.5M $SrCl_2$ were poured into the two limbs on to the gel prepared according to Equation 2. The experimental conditions used for crystal growth are given in Table I.

The calcium and strontium content in the crystals was estimated using atomic emission spectrometry while the iron content in the crystals and in the starting materials was determined using atomic absorption spectrometry. The lattice parameter along the b-axis and the density of the crystals were determined using X-ray diffraction and fluid flotation techniques, respectively. The micromorphology of the as-grown and etched surfaces was examined under an optical microscope.

3. Results and discussion

3.1. Crystal growth and their habit

Crystal growth in single-tube system was carried out using gel of density $1.04\,\mathrm{g\,cm^{-3}}$ in both neutral and bottom layers in two series of experiments. In the first, the pH of the bottom gel layer was 5.3, while in the other it was 6.5. However, the initial pH of the neutral gel was kept at 5.3 in both bases. In the two-layer single-tube system, crystal growth was conducted at pH 5.3, 6.2 and 6.5. The gelling time for the gel at pH values of 5.3 and 6.5 was about 4 days, while for pH 6.2 it was about 10 days. Gelling and growth was conducted at 25° C. In the two-layer single-tube system nucleation was observed immediately after adding the chloride solution at the solution–gel interface, but in the three-layer system it was observed after 2 days. The crystals were extracted from the tubes after 4 weeks. Some of the crystals grown are shown in Fig. 2.

In the U-tube system, crystal growth was carried out at different pH values, but growth was observed only at pH 4.2. This is understandable because the maximum specific volume of the pores of this silica gel is actually observed at pH greater than 4 [11–13].

Growth of a well-defined habit (Fig. 3) was observed to take place in the bottom layer of the three-layer system. However, crystals grown near the boundary of the two layers of the gel were somewhat more elongated than those grown away from it.

3.2. Composition of the crystals

It was found that the composition of the mixed crystals grown along the length of the bottom layer was different. For example, in the case of three-layer system with pH 5.3 in the bottom and middle layers, using 0.5M $CaCl_2$ + 0.5M $SrCl_2$, the molar content of Ca^{2+} in crystal grown at distances of about 2 and 4 cm away from the boundary of the two gel layers was 0.54 and 0.56, respectively. In the case of the system with pH 6.5 of the

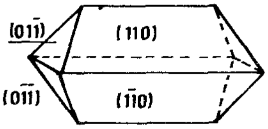

Figure 3 Schematic illustration of the habit of the mixed crystals.

TABLE I Conditions of crystal growth by the single-tube method and characteristics of the grown crystals

Growth conditions			Characteristics of crystals			
Gel		Top solutions (30 cm^3)	Molar fraction Ca	Fe (ppm)	Density (g cm^{-3})	*b*-axis (nm)
Bottom layer	Middle layer					
0.5M SMS* and Wofatit KPS† and 1M H_2Tr pH = 5.3 t = 96 h	0.5M SMS and Wofatit KPS pH = 5.3 t = 96 h	0.1M $CaCl_2$ and 0.9M $SrCl_2$	0.14	6	2.0257	1.0822
		0.2M $CaCl_2$ and 0.8M $SrCl_2$	0.24	7	1.9950	1.0782
		0.4M $CaCl_2$ and 0.8M $SrCl_2$	0.44	9	1.9500	1.0710
		0.5M $CaCl_2$ and 0.5M $SrCl_2$	0.54	10	1.9119	1.0662
		0.6M $CaCl_2$ and 0.4M $SrCl_2$	0.64	7	1.8985	1.0631
		0.8M $CaCl_2$ and 0.2M $SrCl_2$	0.84	11	1.8580	1.0571
		0.9M $CaCl_2$ and 0.1M $SrCl_2$	0.94	11	1.850	1.0542
0.5M SMS and Wofatit KPS and 1M H_2Tr pH = 6.5 t = 96 h	0.5M SMS and Wofatit KPS pH = 5.3 t = 96 h	0.2M $CaCl_2$ and 0.8M $SrCl_2$	0.17	8	2.0120	–
		0.4 M $CaCl_2$ and 0.6 M $SrCl_2$	0.38	9	1.9800	–
		0.5M $CaCl_2$ and 0.5M $SrCl_2$	0.46	9	1.9620	–
		0.6M $CaCl_2$ and 0.4M $SrCl_2$	0.53	8	1.9440	–
		0.8M $CaCl_2$ and 0.2M $SrCl_2$	0.78	11	1.8690	–
		0.9M $CaCl_2$ and 0.1M $SrCl_2$	0.83	12	1.8600	–
0.86M SMS and 1M H_2Tr pH = 6.2 t = 240 h	–	1M $CaCl_2$	1	–	1.823	1.0517
		1M $SrCl_2$	0	–	2.052	1.0862

TABLE I Continued

0.5M SMS and 1M H_2Tr pH = 5.3 $t = 96$ h	–	0.5M $CaCl_2$ and 0.5M $SrCl_2$	0.56	14	–	–
pH = 6.5		0.5M $CaCl_2$ and 0.5M $SrCl_2$	0.53	13	–	–

*SMS – sodium metasilicate.
†Wofatit KPS – cation exchanger.

bottom layer, the molar concentration of Ca^{2+} in crystals grown at about the same distance was 0.46 and 0.42, respectively. Hence, in order to compare the composition of the mixed crystals, crystals grown at a distance of about 2 cm from the gel–gel interface were used.

A graph of the dependence of mole fraction of Ca^{2+}, x(M), and Sr^{2+}, $(1-x)$(M) in the lattice of mixed crystals on the concentrations, x(M), of $CaCl_2$ and $(1-x)$(M) of $SrCl_2$ in the top solution layer in the three-layer system is shown in Fig. 4. The data of Patel and Arora [8, 9] for crystals grown in the beaker system are also shown in the figure. It may be noted that the dependence reported by Patel and Arora [8, 9] is essentially linear, but in our three-layer system there is a deviation from linear dependence. In the case of crystals grown at pH 5.3 in the middle and bottom layers, the molar concentration of Ca_2^{2+} is always higher than that in the top solution layer. However, in crystals grown at pH 5.3 in the middle layer and pH 6.5 in the bottom layer the molar concentration of Ca^{2+} is always less. This may be explained in terms of ionic exchange between the hydrogen ions of the OH^- group present on the gel surface and the Ca^{2+} ions selectively adsorbed on it. This exchange can take place only at a sufficiently high pH [14], since it requires the dissociation of weak acidic groups.

3.3. Iron content in the crystals

Most of the crystals grown exhibited a yellowish appearance as a consequence of the incorporation into the lattice of iron contained in sodium silicate (5 ppm), tartaric acid (8 ppm) and in $CaCl_2$ (6 ppm) and $SrCl_2$ (< 0.5 ppm), the last two being employed as the feed solution. The results are listed in Table I. It may be seen that:

(1) in crystals of different composition growing at the same pH, more iron is incorporated in crystals containing more Ca. This may be attributed to the higher iron content in $CaCl_2$;

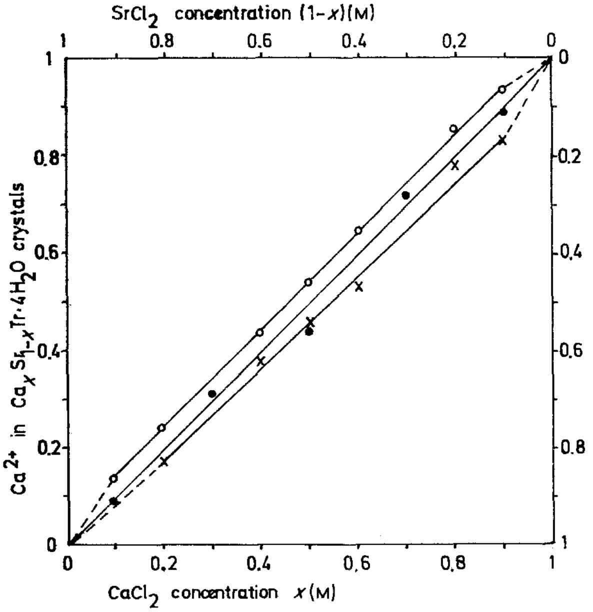

Figure 4 A plot of the dependence of molar fraction of Ca^{2+} in the lattice of crystals on the concentration of $CaCl_2$ in the top solution of the three-layer system: ○ – gel pH 5.3, X – gel pH 6.5, and ● – data of Patel and Arora [8, 9].

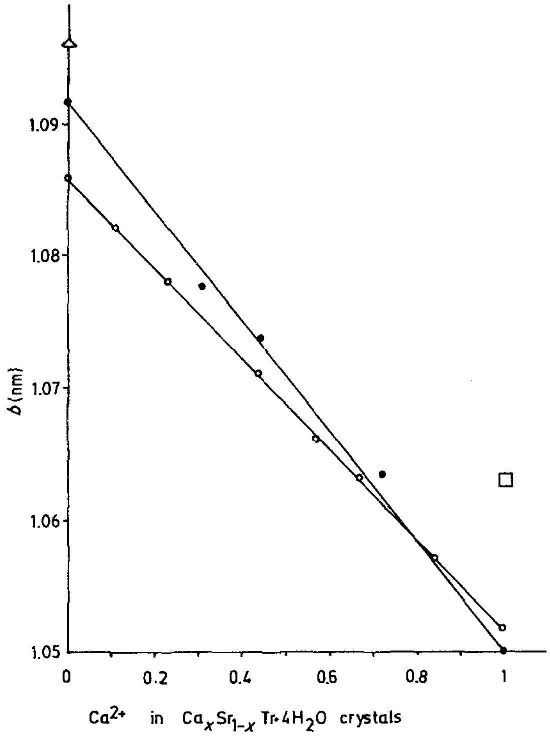

Figure 5 A plot of the variation in *b*-axis with the concentration of cations present in the crystal lattice: ○ – present data, ● – data of Patel and Arora [8, 9], □ – Evans [15] and △ – Bohandy [2].

(2) in systems having a neutral layer, the iron content is less. This may be explained in terms of the higher affinity of the middle layer towards cations of higher charges.

3.4. Lattice parameter

The lattice parameter of the mixed crystals along the *b*-axis follows Vegard's law (Fig. 5) and may be expressed by the empirical relation:

$$b(Ca_x\,Sr_{1-x}Tr \cdot 4H_2O) = 10.8603 - 0.3453\,x.$$

The results obtained by Patel and Arora [8, 9] for needles, also included in Fig. 5, show a somewhat higher value of *b* for the mixed crystals and for $SrTr \cdot 4H_2O$ and a smaller value for $CaTr \cdot 4H_2O$. A higher value of both individual calcium and strontium tartrate crystals has also been reported [2, 3, 15, 16]. These anomalies are probably associated with the quality of the crystals.

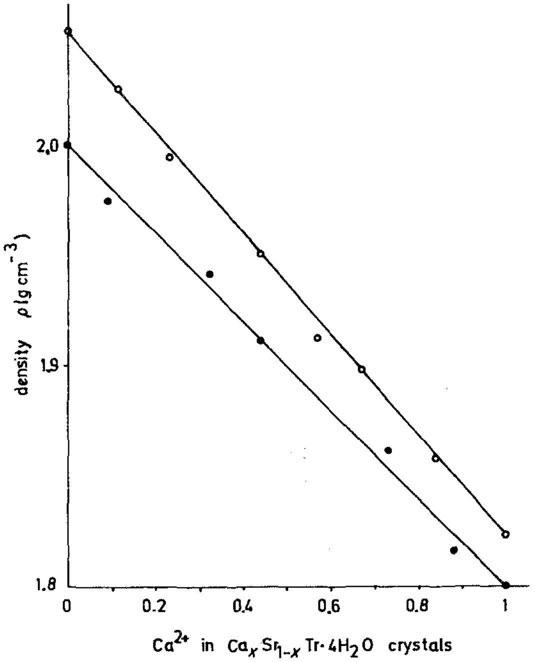

Figure 6 A plot of the variation in density, ρ, of crystals with the concentration of cations present in the crystal lattice: ○ – present data, and ● – data of Patel and Arora [8, 9].

3.5. Crystal density

The density, ρ, of the crystals as a function of Ca^{2+} and Sr^{2+} content in the lattice of mixed crystals is shown in Fig. 6. The data of Patel and Arora [8, 9] for needles picked up from just below the gel–solution interfaces are also presented in the figure. As found by Patel and Arora [8], although the dependence of ρ on composition is linear, the values of the density of our crystals is always higher than those for

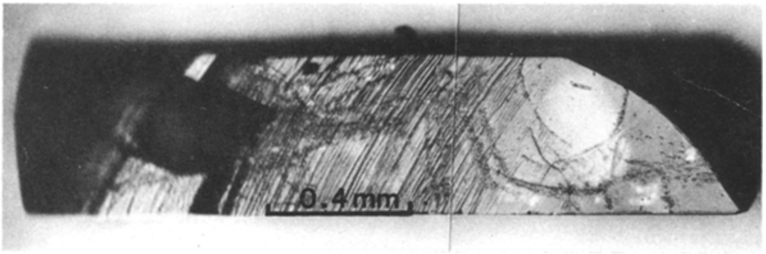

Figure 7 As-grown (1 1 0) surface of a mixed crystal.

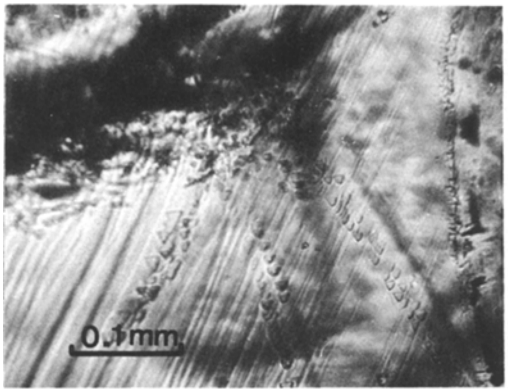

Figure 8 Etch pits on the as-grown (1 1 0) surface of a mixed crystal and liquid inclusions.

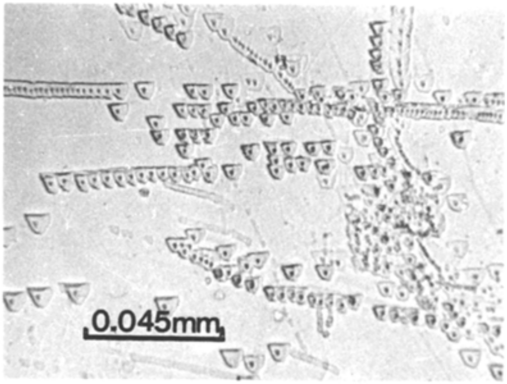

Figure 9 Etch pit pattern on the (1 1 0) surface of a mixed crystal after successively etching for 15 sec in water and for 10 sec in formic acid.

needles and can be expressed by the empirical relation:

$$\rho(\mathrm{Ca}_x\,\mathrm{Sr}_{1-x}\,\mathrm{Tr}\cdot 4\mathrm{H_2O}) = 2.0516 - 0.2242\,x.$$

There are two possible reasons for this discrepancy. Firstly, the needles contain solution inclusions or are hollow, as is well known for needles grown from solution [17]. Secondly, the measurement of crystal density using a picnometer is less accurate [18].

3.6. Micromorphology of as-grown and etched surfaces

Fig. 7 illustrates an example of the as-grown (1 1 0) surface of a mixed crystal. It shows parallel layers initiating from the crystal corner. The layers are thin in the beginning but become progressively thicker as they move away from the initiation centre. In addition, small triangular etch pits may be observed on the surface. Fig. 8 shows another example of the (1 1 0) as-grown surface of the above crystal, where triangular etch pits are clearly seen. By focusing the microscope below the surface, it was established that immediately below the etch pits, liquid inclusions appear in the crystal.

Fig. 9 shows the surface of a crystal photographed after etching successively first in water and then in formic acid for 15 and 10 sec, respectively. The fact that formic acid produces etch pits on almost every pit produced by water, may be taken to imply that both water and formic acid locate the emergence points of dislocations on the (1 1 0) surface.

Water and formic acid also reveal dislocations emerging on other faces of the pure and doped crystals. The etch pits formed on the (0 1 1) face are elongated triangular (Fig. 10), while those produced on the (0 1 0) face are elongated elliptical.

Finally, it may be mentioned that water and formic acid produce essentially similar etch pits on a particular face of the crystals, but formic acid produces somewhat deeper etch pits. It was found that addition of NH_4Cl to water neither leads to a change in the pit morphology nor in the pit density. In our opinion, addition of NH_4Cl to water to reveal dislocations in tartrates, as done by Patel and Arora [6], is unnecessary.

In the light of the observation of layers, it is believed that the growth of crystals in the gel is by the layer growth mechanism, but the etch pits are produced at dislocation sites during the act of rinsing the crystals in water in order to remove the gel sticking to a surface.

4. Conclusions

(1) The use of a middle gel layer enables the

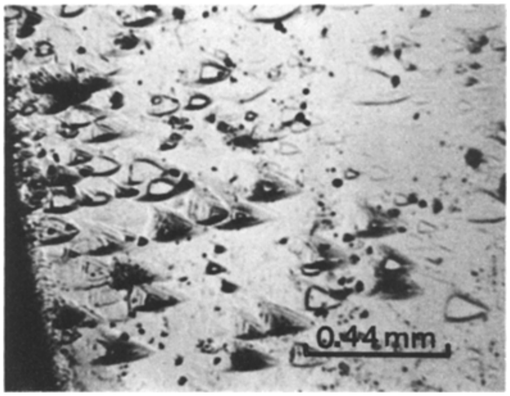

Figure 10 Triangular etch pits formed on the (0 1 1) face of strontium tartrate tetrahydrate crystal by exposure to water for 15 sec.

growth of good-quality crystals of tartrates in silica gel.

(2) In a U-tube, crystal growth takes place only at gel pH 4.2. This is probably associated with the formation of gel of a suitable pore size.

(3) Selective adsorption of Ca^{2+} ions in gel of a sufficiently high pH leads to a change in the incorporation of calcium in the lattice of mixed crystals.

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