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Growth and SEM & XES characterization of calcite and KDP single crystals grown by the gel method

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ABSTRACT. The growth of calcite and KDP crystals by the gel technique using purified industrial sodium silicate is reported. Chemical analysis, optical and scanning electron microscopy and microprobe studies were used for their characterization. This study shows that purified industrial sodium silicate is suitable to prepare good quality gels useful for crystal growth. Crystals of rhombohedral and prismatic habit for calcite and KDP, respectively, were obtained. In the case of calcite the crystals show surface inhomogeneities which have been associated with the presence of chlorine, silicon and sodium. The KDP crystals display an almost smooth surface, and impurities of chlorine, sodium and aluminium were found in this case. Some detected impurities were already present in the nutrient solutions.

RESUMEN. Se reporta el crecimiento de cristales de calcita y KDP mediante la técnica de gel, usando silicato de sodio industrial purificado. La caracterización se realizó mediante análisis químico, microscopía óptica y electrónica de barrido y microsonda. Este trabajo muestra que el silicato de sodio industrial purificado es adecuado para preparar geles de buena calidad que pueden ser utilizados como medio para el crecimiento cristalino. Se obtuvieron cristales con hábito romboédrico y prismático para la calcita y el KDP, respectivamente. En el caso de la calcita, los cristales presentan inhomogeneidades superficiales que asociamos a la presencia de cloro, silicio y sodio. Los cristales de KDP muestran una superficie casi uniforme y las impurezas encontradas en este caso fueron cloro, sodio y aluminio. Algunas impurezas detectadas estaban presentes en las soluciones nutrientes.

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1. INTRODUCTION

The gel growth method offers in a simple and inexpensive way the possibility to control parameters such as temperature and specially the velocity of nucleation, difficult to maintain in other methods [1, 2]. The purpose of the present work is to test if industrial sodium silicate (liquid glass) can be used to prepare gels with mechanical properties useful for crystal growth and with a minimum of impurities.

We choose calcite and KDP to be grown in the prepared gels, because their growth has been reported in the literature, using reactive grade chemicals to prepare the gel media [3, 4]; and because calcite has well-known applications in optical instrumentation [5] while KDP crystals are being used as an essential part of electro-optic modulators [6] and since 1990 as lasers [7].

2. EXPERIMENTAL PROCEDURE

2.1. Purification of sodium silicate

Industrial sodium silicate is a solution of Na_2O and SiO_2 approximately in a 1:3.3 proportion, with a density 1.4 g/ml and a yellowish colour. The solution was purified by passing it through a column packed with purified natural montmorillonite $(Al, Mg)_2Si_4O_{10}(OH)_2$ $4H_2O$, proceeding from a region near Puebla; after passing through the column the liquid glass is already clear and the characterization of sodium silicate is done by means of measurements of density, alcalinity, SiO_2 content and quantification of impurities such as Al_2O_3, Fe_2O_3, CaO and MgO [8].

2.2. Crystal growth

By adding drop by drop purified sodium silicate ($\rho = 1.06$ g/ml) to acetic acid (1M) in a 1:1 proportion it was possible to obtain a clear gel useful to be used as medium to grow calcite crystals. Solutions of $CaCl_2$ and Na_2CO_3 are introduced in a test tube containing the gel, first the calcium solution and 24 hours later that of sodium carbonate. Several concentrations of both solutions were tried (10%, 20%, 30%, 40%, 50%, 60%, 70% and saturated), finding that concentrations between 30 and 38% produce the biggest crystals. Calcium carbonate (calcite) is obtained according to the following reaction: $CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$.

In the case of KDP (KH_2PO_4), the two layer method [5] was used. The first gel layer was prepared using a supersaturated solution of KDP (at 45°C) to which the solution of purified sodium silicate is added ($\rho = 1.06$ g/ml) in a 2.4:1 proportion, respectively. Twenty-four hours later a second gel layer is prepared with acetic acid (1M) and purified sodium silicate (same density as in the first layer) in a 1:1 proportion, 48 hours later dry ethanol (10 mls) is introduced in this layer by means of a syringe, in order to diminish the solubility of KDP to start the growth process.

3. RESULTS AND DISCUSSION

Table I shows the data concerning the chemical analysis of purified industrial sodium silicate, compared with those reported for the reactive grade reagent. The higher content of Na_2O, SiO_2 and Al_2O_3 in the purified sodium silicate could be due to the passage through the montmorillonite column.

Fig. 1 exhibits the optical micrographs of the crystals reported here. The obtained calcite single crystals using solutions with a concentration of 38% Fig. 1(a) are turbid and have typical rhombohedral habit, with a size as large as $1.5 \times 1.5 \times 1.5$ mm^3. KDP single crystals are shown in Fig. 1(b), these crystals have an habit formed by prismatic (001) and pyramidal (101) faces, as large as $19.8 \times 5 \times 2.8$ mm^3, almost all of them contain in the center a halo probably due to incorporation of the gel media during the growth process.

Plotted in Fig. 2 are typical growth rate measurements for both crystals. A small crystal

TABLE I. Chemical analysis of sodium silicate.

	Reactive grade*	Purified
Density (g/ml)	1.29	1.40
Alcalinity	0.18	0.17
% Al_2O_3	—	0.51
% SiO_2	25.5 – 28.5	32.2
% Na_2O	7.5 – 8.5	7.9 – 10.3

*Merck-catalog.

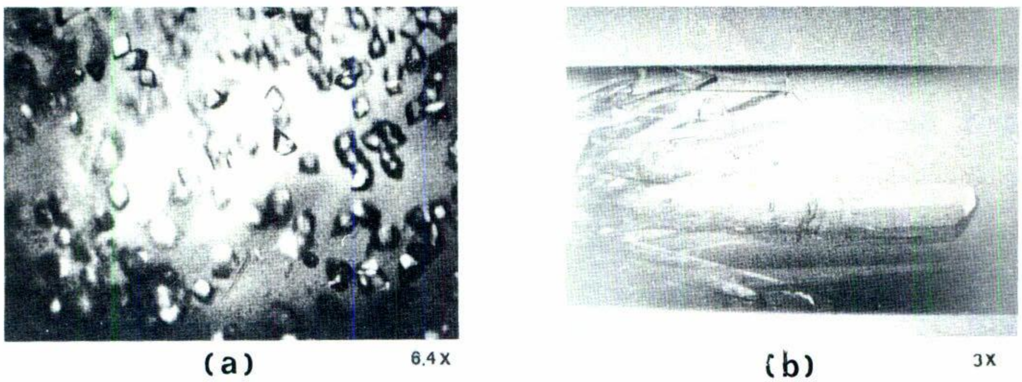

FIGURE 1. Optical micrographs of (a) calcite and (b) KDP crystals.

size and a slow growth with tendency to saturation after 50 days is observed in Fig. 2(a) for calcite, while for KDP crystals Fig. 2(b) it can be observed a big crystal size and a rapid growth, in this case the saturation tendency appears after 25 days.

The quality of single crystals may be assessed with a polarizing microscope, between crossed polarizers good quality single crystals should show a sharp extinction, *i.e.*, by rotating the crystal about the axis of the microscope, extinction should occur homogeneusly throughout the entire crystal [9].

Figs. 3 (a) and (b) show calcite and KDP crystals, respectively, one in extinction and the other in diagonal positions (at nearly 45° each other, in order to be able to obtain the photographs); the uniformity of extinctions proofs the good quality of our single crystals.

SEM-micrographs of the grown crystals taken with a JEOL JSM-35C microscope are displayed in Figs. 4 and 5. Fig. 4(a–d) gives the surface morphology for calcite single crystals grown under different conditions. Strong surface irregularities were observed when the concentration of both nutrients was 30% Fig. 4(a). From the Fig. 4(b) it is evident that the surface quality was increased with the increasing percentage of both nutrients to 38%.

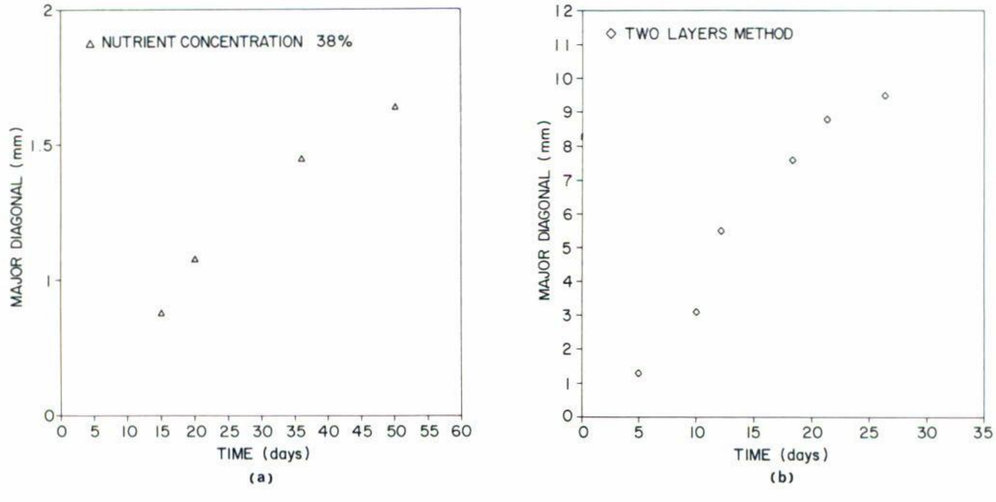

FIGURE 2. Growth rate measurements for (a) calcite and (b) KDP crystals.

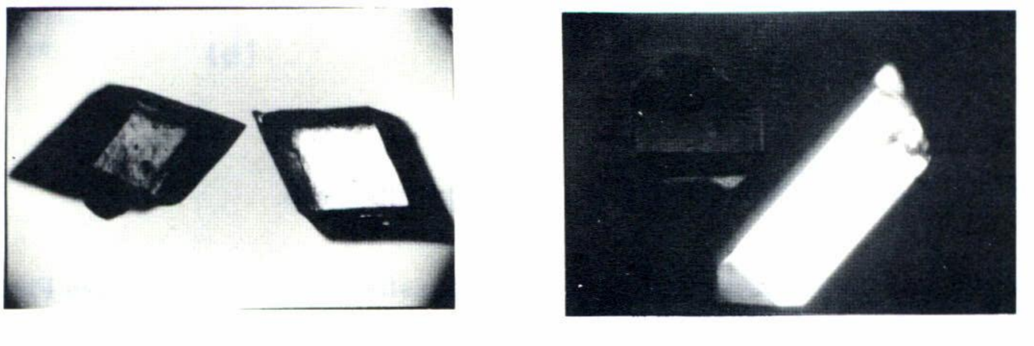

FIGURE 3. Optical micrographs of (a) calcite and (b) KDP crystals between crossed polars.

Fig. 4(c, d) shows an almost smooth surface for crystals grown adding small quantities of NaOH to neutralize the H_2CO_3 formed during the gelling process as discussed by Henisch [1]. Fig. 5 exhibits KDP single crystals with typical habit: prismatic and pyramidal faces, some surface irregularities can be observed in both cases.

In order to study the stoichiometry of the crystals, XES analysis were made at different points on the crystals surface with a Kevex Micro-X 7000 system. $CaCO_3$ and KDP reactive grade were used as standards. Tables II and III summarize the results obtained by microprobe on different regions of the crystals shown in Figs. 4 and 5. In the case of calcite crystals grown using a 30% concentration of nutrients Fig. 4(a), chlorine, silicon and sodium in a rather high percentage were detected. No impurities were detected for calcite

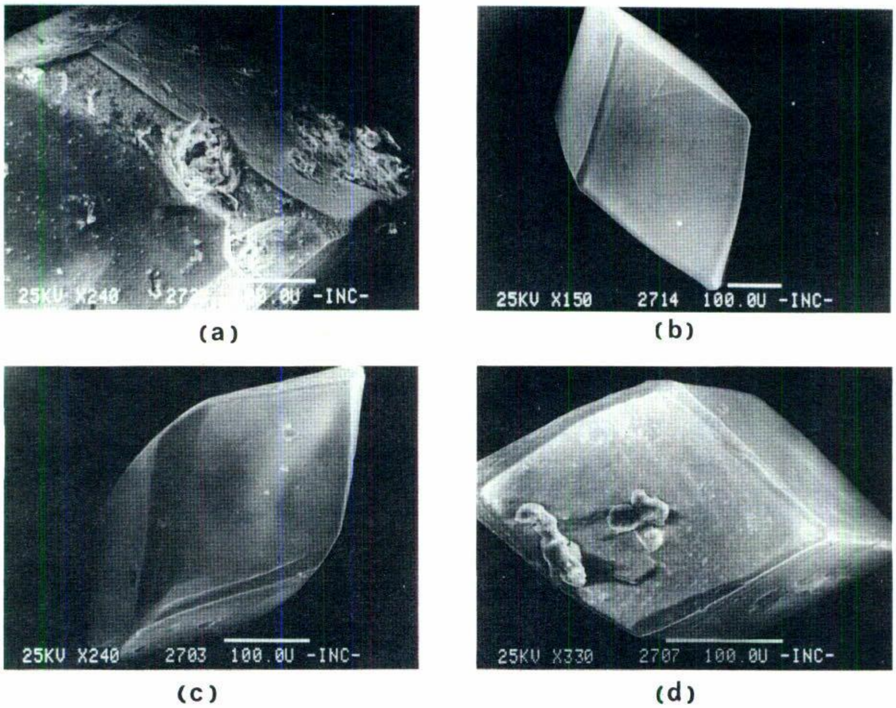

FIGURE 4. SEM micrographs of calcite crystals. (a) and (b) surface morphology for crystals grown with 30% and 38% of nutrients, respectively. (c) and (d) show crystals grown adding small quantities of NaOH to the nutrients 38% concentrated.

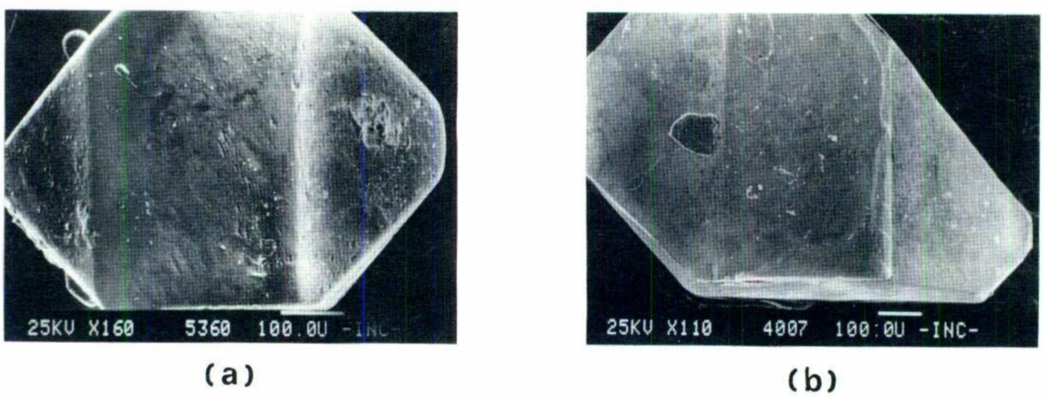

FIGURE 5. Photomicrographs of KDP single crystals showing (a) surface morphology and (b) typical habit with prismatic and pyramidal faces.

Table II. Microprobe analysis of calcite single crystals.*

Nutrients	Crystal	Element (% Atomic)			
	Fig. 3	Ca	Si	Cl	Na
30%	(a)	39.02	0.99		
"	(a)	38.78	1.20		
"	(a)	39.83			
"	(a)	29.38	1.98	7.20	1.47
38%	(b)	40.00			
38%+NaOH	(c)	38.46	0.61	0.97	
38%+NaOH	(d)	21.92	1.22	13.22	
	(d)	39.93	0.87	0.24	

*Theoretical Ca contain = 40.04.

Table III. Microprobe analysis of KDP single crystals.*

Crystal	Element (% Atomic)				
Fig. 4	K	P	Na	Al	Cl
(a)	30.21	24.93	0.36		0.49
(a)	28.48	22.91			
(a)	28.86	22.20			
(b)	28.16	22.95			
(b)	28.33	22.58		0.19	
(b)	28.30	22.79			
(b)	31.08	20.29			

*Theoretical K and P contain = 28.73% and 22.76% respectively.

crystals grown using a 38% concentration of nutrients Fig. 4(b). For this concentration and adding small quantities of NaOH Fig. 4(c, d) no impurities of sodium were detected, the detected percentages of silicon were like those found for crystals obtained using 30% concentration of nutrients. A percentage of chlorine higher than that for crystals obtained using 30% concentration of nutrients was detected only in one case. KDP crystals surface show also the presence of Cl and Na Fig. 5(a) but, with low percentages. Impurities of Al are present on crystal displayed in Fig. 5(b).

Comparing our results with the few reports on impurities content in gel grown crystals, they agree with those concerning silicon content, where it has been found a content between 0.45 and 1.7% [1]; magnesium [1] and iron [10] where not found in our crystals.

4. Conclusions

It is possible to use with good success purified industrial sodium silicate to prepare gels suitable for crystal growth. The grown single crystals show the characteristic habit, *i.e.*, rhombohedral for calcite and prismatic for KDP.

Turbidity observed in both type of crystals, in the bulk for calcite and forming an halo in the center for KDP, confirms that the inclusion of Si occurs in the initial stages of the growth.

All surface irregularities observed on the crystals are associated with the presence of impurities —silicon, chlorine, sodium and aluminium—, some of them already present in the nutrient solutions. Further work is in progress to improve the purification of sodium silicate.

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