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Microtopographical and Raman spectral studies on calcium sulphate dihydrate (gypsum) crystals grown in silica gel in the presence and absence of barium chloride as additive.

P. KUMARESON, S. DEVANARAYANAN
Department of Physics, University of Kerala, Kariavattom, Trivandrum, 695 581, India

A procedure for the growth of calcium sulphate dihydrate (gypsum) crystals, $CaSO_4 \cdot 2H_2O$, by a gel technique in the presence of barium chloride as an additive as well as without the additive, is described. Optimum conditions for the growth of good quality crystals are worked out. Needle-shaped crystals with well-defined prism faces are obtained. Microtopographical studies of the crystals are carried out. The observed surface structures on the prism faces of the crystals include vertical striations and parallelogram-shaped, oriented growth hillocks. Etch patterns on these faces are described and discussed. Reciprocity of the growth and etch mechanisms is established. Laser Raman spectral studies of these crystals are also made. Splitting of the non-degenerate fundamental is observed in the spectrum of the crystals grown in the presence of the additive. The present studies indicate that the additive used enhances the quality of the crystals.

1. Introduction

Calcium sulphate dihydrate crystals (gypsum), apart from their use as a building material, find applications in geothermal methods and petroleum drilling technology. In processes like waste water treatment, desalination and the industrial production of phosphoric acid these crystals are the subject of widespread interest. It is well known that macroscopic crystals with high perfection can be obtained by the gel technique [1]. Van Rosmalen *et al.* [2] have shown that the presence of sodium chloride as an additive further enhances the degree of perfection of gel-grown calcium sulphate crystals. In the present work attempts have been made to grow large crystals of gypsum with improved quality in a gel medium in the presence of barium chloride as additive. Microtopographical studies of surface structures and laboratory-produced etch patterns on the prism faces of the crystals grown have been carried out. Laser Raman spectral studies have also been made for characterization and obtaining qualitative information on the crystals grown.

2. Experimental details

Crystals of calcium sulphate were grown in U-tubes (20 mm diameter and 150 mm high) at room temperature (30° C). AR grade sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) of specific gravity 1.05 was gelled at pH 8, using 20 vol % AR grade sulphuric acid which acted as the inner reactant. After gelation, an optimum ageing of 24 h was found to be suitable to get a sizeable number of crystals evenly distributed in the vicinity of the gel–solution interface. For the growth of crystals in the presence ofthe additive the outer electrolyte was an aqueous mixture of $CaCl_2$ (1 M) and $BaCl_2$ (0.5 M). 15 ml of this mixture was poured in one of the limbs of the U-tube. $BaCl_2$ was the additive. The other limb contained 15 ml of 20 vol % AR grade sulphuric acid. Needle-shaped crystals started growing after a week and the growth process continued for three more weeks. Fully grown crystals (0.5 mm diameter and 15 mm length) were carefully removed from the gel, washed immediately with acetone, dried and stored in a moisture-free chamber.

A similar procedure was adopted for the growth of

Figure 1 Vertical striations on a prism face of an AP crystal (× 200).

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Figure 2 Densely populated, oriented, parallelogram-shaped growth hillocks on the prism face of AP crystal (× 250).

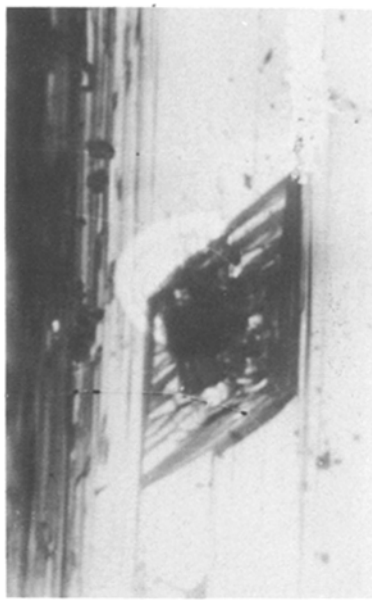

Figure 4 An isolated parallelogram-shaped growth hillock on a prism face of an AP crystal (× 400).

crystals in the absence of the additive. In this case the outer electrolyte contained $CaCl_2$ alone.

In this paper crystals grown in the presence of the additive and those grown in the absence of the additive are referred to as AP and AA, respectively.

3. Observations and results

3.1. Surface structures

The habit prism faces of the crystals were examined under an optical metallurgical microscope and photomicrographs were taken.

3.1.1. AP crystals

Smooth, fully developed and fairly large prism faces of the crystals were noticed. On these faces, smooth and vertical striations were observed (Fig. 1). On some faces densely populated, oriented and parallelogram-shaped growth hillocks were noticed (Fig. 2). Fig. 3 shows one such hillock at a higher magnification. Some prism faces revealed the presence of isolated, oriented growth hillocks (Fig. 4). On some growth pyramids, growth layers composing the pyramid were distinctly visible (Fig. 5). The dark regions observed at the initiation centres of the big hillocks might be due to aggregate crystals or impurities.

3.1.2. AA crystals

Densely populated, oriented and parallelogram-shaped growth pyramids were noticed on the fully developed and fairly large prism faces of these crystals (Fig. 6). Some isolated growth pyramids are shown in Fig. 7.

3.2. Etch patterns

Both AP and AA crystals were etched in distilled

Figure 3 Region of Fig. 2 showing growth hillock at a higher magnification, revealing growth layers composing the hillock (× 750).

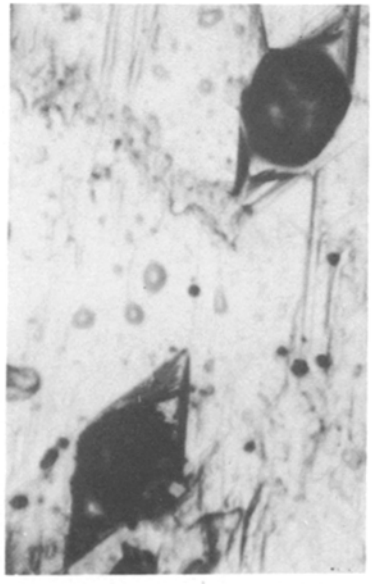

Figure 5 Two oriented, parallelogram-shaped growth hillocks with bulk impurity at the initiation centre, and tiny growth hillocks with distinct growth layers on a prism face of an AP crystal (× 200).

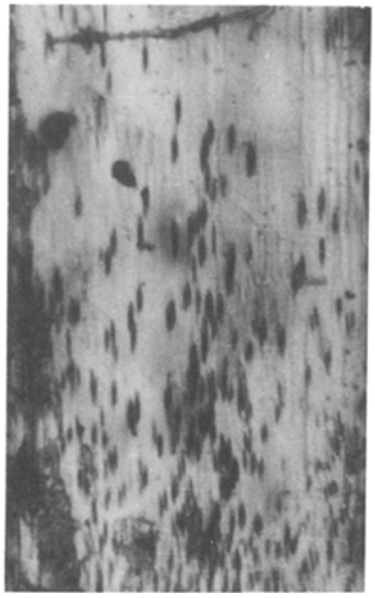

Figure 6 Densely populated, oriented, parallelogram-shaped growth hillocks on a prism face of an AA crystal (× 100).

water at room temperature (30° C) for 2 h. The etch patterns produced on the prism faces were studied under a scanning electron microscope (Model S4-10) and scanning electron micrographs were taken.

3.2.1. AP crystals

Smooth vertical striations and some impurities were distinctly seen. The regions between striations were devoid of etch pits and were reasonably smooth and plane (Fig. 8). Very rarely at some regions of the prism face, oriented, parallelogram-shaped pits were observed. The longer sides of the pits were parallel to the vertical striations. Further, the pits were much longer along the vertical direction (Fig. 9).

3.2.2. AA crystals

The prism faces of AA crystals consisted of densely populated, oriented, parallelogram-shaped etch pits.

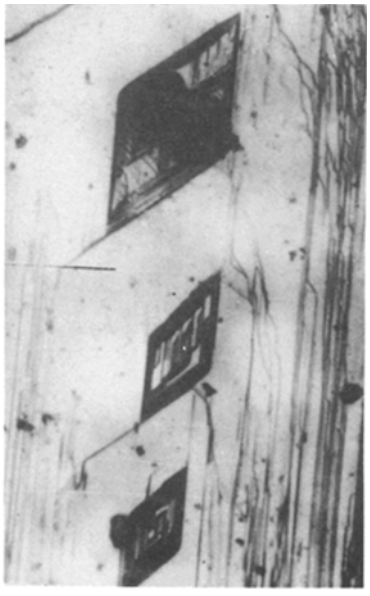

Figure 7 Well-defined isolated growth hillocks on a prism face of an AA crystal (× 200).

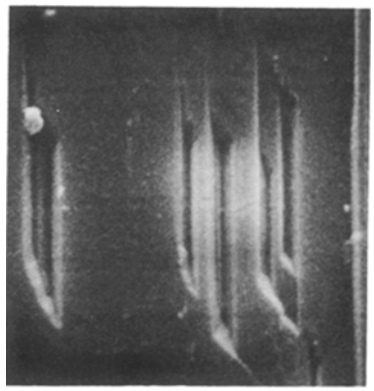

Figure 8 Smooth striations on a prism face of an AP crystal after etching (× 600).

The neighbouring pits intergrow forming some irregular patterns in some regions of the face (Fig. 10). An isolated eccentric pit is shown in Fig. 11.

3.3. Raman spectral studies

Laser Raman spectra of both AP and AA crystals were recorded under identical conditions of experimentation with the help of an SPEX Ramalog spectrophotometer, equipped with 1401 double monochromator. The 165 Ar^+ laser line (514.5 nm) was used as the excitation source. The recorded Raman spectra of AP crystals (full lines) and of AA crystals (dotted lines) are given in Fig. 12. The observed peaks corresponding to AP crystals are much sharper and more intense as compared to those of the AA crystals. The vibrational frequencies and their assignments are listed in Table I.

4. Discussion

The observed fully developed and fairly large prism faces of the crystals may be considered to be slowly growing faces.

The presence of parallelogram-shaped growth hillocks indicates that there is independent growth on the prism faces. The symmetry of these growth hillocks confirms the symmetry of the prism faces on which they occur. Such growth pyramids indicate that a large number of nucleation centres remain active till the end of the growth of the face.

The vertical sides of the parallelogram-shaped growth hillocks constitute vertical striations parallel

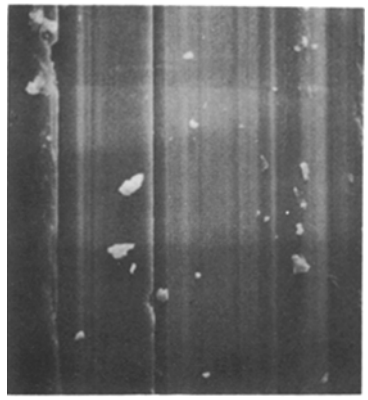

Figure 9 Oriented parallelogram-shaped etch pits on a prism face of an AP crystal (× 1200).

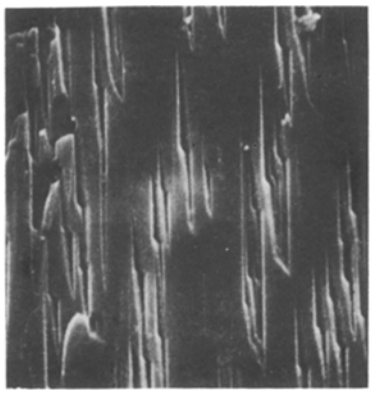

Figure 10 Densely populated, oriented, parallelogram-shaped etch pits on a prism face of an AA crystal (× 1200).

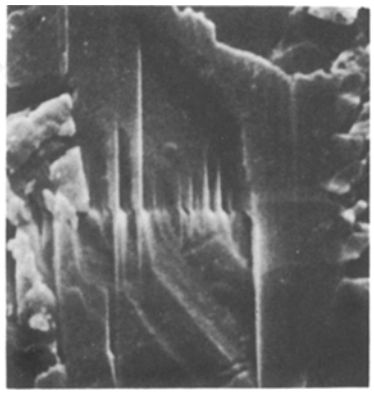

Figure 11 An eccentric etch pit on the prism face of an AA crystal (× 1200).

to the edge of intersection of two neighbouring prism faces of the crystal. The smoothness of such striations is indicative of an unhindered advance of growth fronts of growth layers comprising the growth hillocks. The observed elongation of the parallelogram shapes of the growth hillocks along the morphological *c* axis [2] indicates a higher growth rate along this direction when compared to that of the lateral growth. The observed closely spaced striation is due to the high rate of spreading of growth layers.

These observations prove that the crystals in general, and the prism faces in particular, have grown by a two-dimensional nucleation mechanism, namely the spreading and piling up of growth layers.

The etch pits produced on the prism faces are well defined, parallelogram-shaped, and oriented with the longer sides parallel to the edge of intersection between neighbouring prism faces. These etch pits have their orientation opposite with respect to that of the growth hillocks on a prism face. As in the case of growth features, the symmetry of the pits confirms the symmetry of the prism face on which they occur. These observations establish the reciprocity of growth and etching mechanism for the prism faces under study.

Some regions of the face between striations, after etching, are remarkably smooth and plane. This is indicative of surface dissolution, quite possibly of monomolecular dimension.

The rectilinearity of the striations, even after etching, can be attributed to the unhindered retreat of etch fronts. The eccentric pit shown in Fig. 11 may be attributed to inclined dislocation. This is confirmed by progressive etching experiments. As observed in the case of growth features, the higher etch rate along the *c* axis explains the elongated parallelogram shapes of the etch pits.

The observed smaller density of pits on the prism faces of the AP crystals, as compared to AA crystals, reveals a higher degree of homogeneity in the growth of the former.

The observed sharper peaks in the laser Raman spectra of the AP crystals and the corresponding broader peaks of the AP crystals indicate a more homogeneous growth of the former [3]. Further, the spectral lines of higher intensity noticed in the case of AP crystals have also been observed by Krishnamurthy and Soots [4] in the laser Raman spectrum of pure oriented single crystals of gypsum for Ag and Bg modes. Hence it is evident that the AP crystals are tending towards perfection. This result is also confirmed by the observed splitting of the non-degenerate fundamental (984 cm^{-1}) into two components (1009 and 994 cm^{-1}) in the case of AP crystals, indicating resonant interaction between SO_4^{2-} ions and their free vibrations.

5. Conclusions

1. Studies on surface structures, etch patterns and laser Raman spectra reveal that crystals of calcium

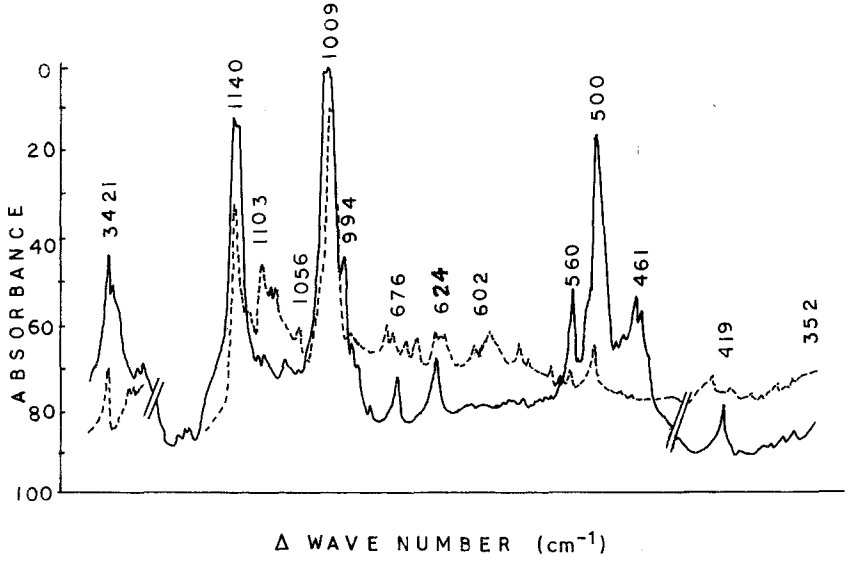

Figure 12 Laser Raman spectra for (——) AP crystals and (– – –) AA crystals.

TABLE I Assignment of Raman lines

Raman frequency (cm^{-1})	Assignment*
461	$\nu_2 SO_4$
500	$\nu_2 SO_4$
60	$\nu_4 SO_4$
994	$\nu_1 SO_4$
1009	$\nu_1 SO_4$
1140	$\nu_3 SO_4$
3421	ν_1, $\nu_3 H_2O$

*ν_1 = Symmetric stretching, ν_2 = symmetric bending, ν_3 = asymmetric stretching, ν_4 = asymmetric bending.

sulphate grown in the presence of barium chloride as additive are of better quality than those grown in the absence of the additive.

2. These crystals grow in a gel medium by a two-dimensional mechanism, namely the spreading and piling up of growth layers.

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