Etching studies on (1 0 0) faces of gel-grown ammonium dihydrogen orthophosphate crystals

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Chemical etching employing specific etchants with varying etch times (20–60 s) has been successfully applied for the first time to reveal dislocation sites on the polished (1 0 0) faces of ammonium dihydrogen orthophosphate single crystals grown at ambient temperature, using a modified gel technique of double diffusion in a U-shaped beaker assembly. The selective behaviour of the etchant for straight and inclined dislocations has been demonstrated. Growth striations due to temperature fluctuations, low-angle tilt boundary and etch channels corresponding to stacking faults were clearly observed. Surface structures of the etched faces were photographed by optical and scanning electron microscopes and are discussed.

1. Introduction

Single crystals of ammonium dihydrogen orthophosphate (ADP) are being utilized extensively in the industrial field as elements of electro-optic (optical modulator) and electro-acoustic devices, in addition to monochromators for X-ray fluorescence analysis. These crystals have been grown by various aqueous solution growth techniques, such as slow evaporation of a supersaturated solution, slow cooling or at a constant temperature [1–3], and also by the gel method [4–6]. Defect characterization using a topographic method [3–5, 7–9] and an etching technique [7] has also been performed for the as-grown crystals. A scan of the literature, however, reveals that only limited work [7] has been reported so far on etching studies of gel-grown ADP crystals. The etching technique is an elegant and simple technique by which to study crystal quality in terms of lattice defects, and the main aim of this report is to present the results of a number of etch-pit studies undertaken on the polished (1 0 0) faces of gel-grown ADP crystals using different etchants with different etch times (20–60 s).

2. Experimental procedure

Large and transparent single crystals of ADP were grown using a slow diffusion process in the silica gel medium by reducing the solubility of the ADP solution incorporated within the gel medium at an ambient temperature in a modified U-shaped beaker assembly [10] as adopted in our laboratory. The gel was prepared by mixing an aqueous solution of sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$, specific gravity $= 1.06\ g\ ml^{-1}$) with a saturated solution of ADP having molarity 3.5 M. After setting the gel in the middle beaker, the reducing agent, ethyl alcohol, was slowly added to each of the two side beakers. This diffuses into the gel and reduces the solubility of ADP and, as a result, nucleation takes place. This optimum growth system, adopted for the first time for growing ADP crystals, yielded crystals of maximum dimensions $42 \times 8 \times 8\ mm^3$ at a gel pH = 4.60 over a period of 4 weeks. Various crystals grown by this improved method have been examined optically. They have grown with their normal habit faces, i.e. with the shape of a tetragonal prism in combination with a tetragonal bipyramid. The perfection of the ADP crystals grown has been studied by the chemical etching technique. Some small crystals were free of dislocations. With the help of metal string-sawing, with water as solvent, specimens of $10 \times 8 \times 8\ mm^3$ were prepared from the as-grown crystals and finally solution polishing was done using a soft felty cloth pasted on a metal disc polisher and wet with a mixture of 50% ethyl alcohol and 50% doubly distilled water, for 15 s. Several specific etchants [7] for revealing dislocations in ADP crystals were used: (1) ferric chloride in HCl added to 80% alcohol–water solution; (2) phosphoric acid in alcohol–water solution; (3) a saturated solution of potassium acid phthalate (KAP); (4) doubly distilled water. Polished specimens were etched in these etchants at an ambient temperature of 27 °C for varying etch times (20–60 s). Etch patterns were observed and photographed under an optical (Carl–Zeiss–Jenavert) and scanning electron (Hitachi-S415A) microscopes.

3. Results and discussion

Fig. 1a–d illustrates the features obtained after etching in etchant 1 for 20, 30, 45 s and 1 min, respectively. During the first etching, after 20 s, a dislocation moved out of a pit and a flat-bottomed pit of (1 0 0) orientation was produced (Fig. 1a). A few pyramidal (symmetrical) pits of different sizes with sides parallel to (1 1 0) resulted after 30 s etching, Fig. 1b. Further

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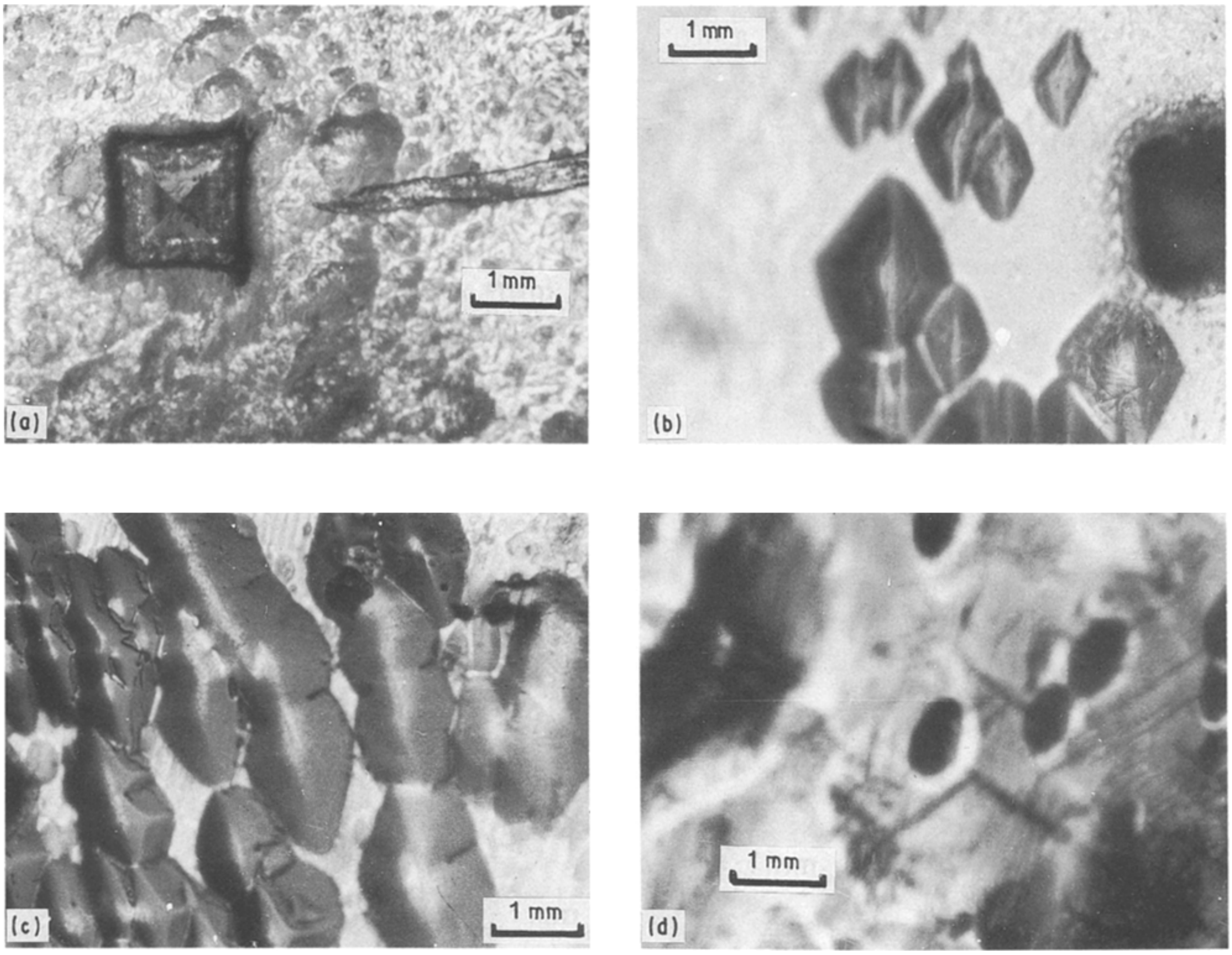


Figure 1 Etch patterns obtained on prismatic faces of ADP using $FeCl_3$ in $HCl + C_2H_5OH$ solution for (a) 20 s, (b) 30 s, (c) 45 s and (d) 60 s etching at 27 °C.

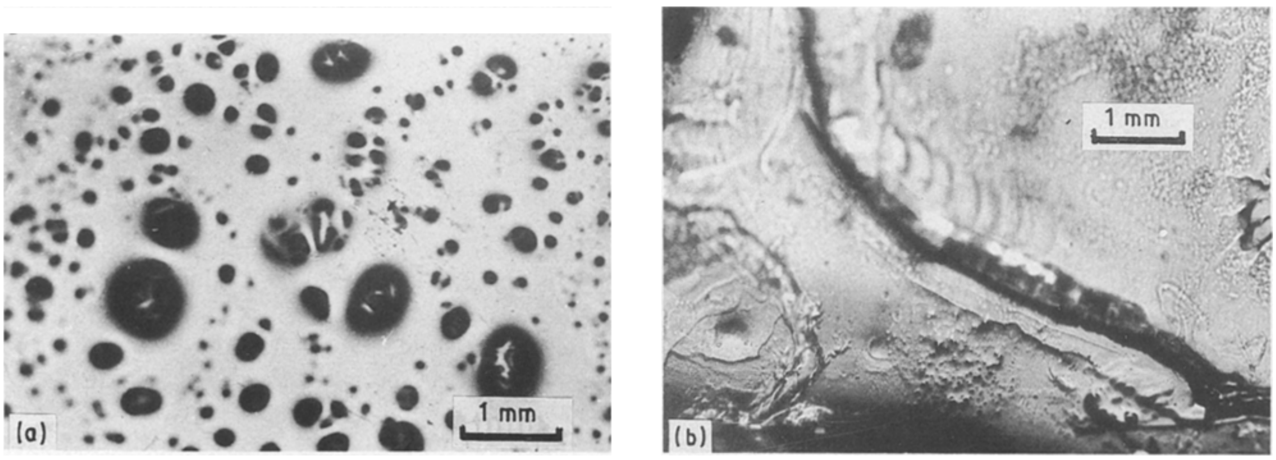
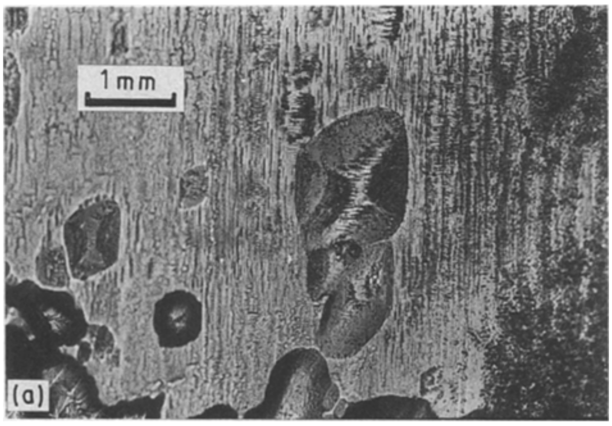
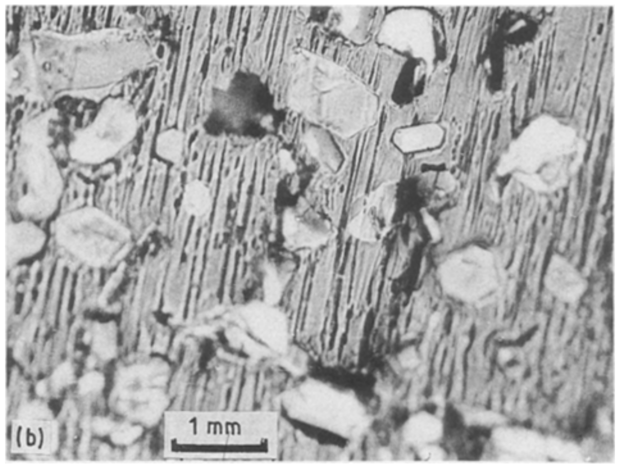


Figure 2 Dislocation etch pits formed on the (1 0 0) face of ADP using H_3PO_4 in 80% C_2H_5OH solution on after (a) 20 s and (b) 30 s etching.

etching for 45 s produced a greater number of slightly asymmetrical etch pits which showed inclined dislocations. Highly inclined dislocations with respect to the surface resulted in smaller etch pits (left side of Fig. 1c) and finally it is evident from Fig. 1d that inclined dislocations produced not only an asymmetrical pit but also brought about a change in the morphology of pits with increasing time. This is probably due to the difference in the dissolution rates at different dislocation sites. Hence the selective behaviour of the etchant with respect to time has shown that at the straight dislocation sites, i.e. perpendicular to the surface, pyramidal pits, and at the inclined dislocation sites, octagonal pits and pits of distorted shapes are produced depending on the degree of inclination.

Fig. 2a and b represent the etch patterns of the (1 0 0) face of ADP etched with the etchant 2. Only impurity clusters and precipitates which are visible in





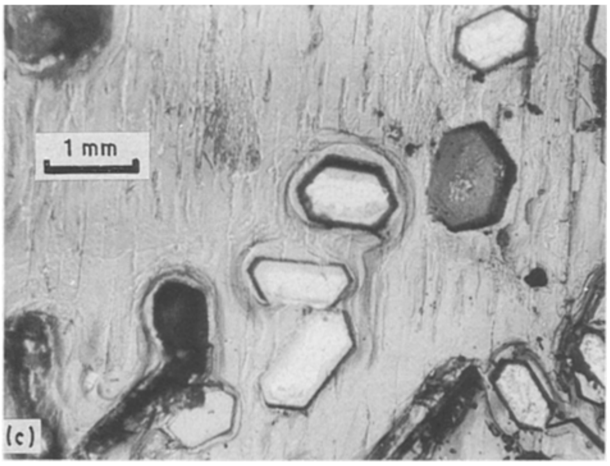


Figure 3 Different morphologies produced on the (1 0 0) face of ADP after etching in KAP solution for (a) 20 s, (b) 30 s and (c) 60 s.

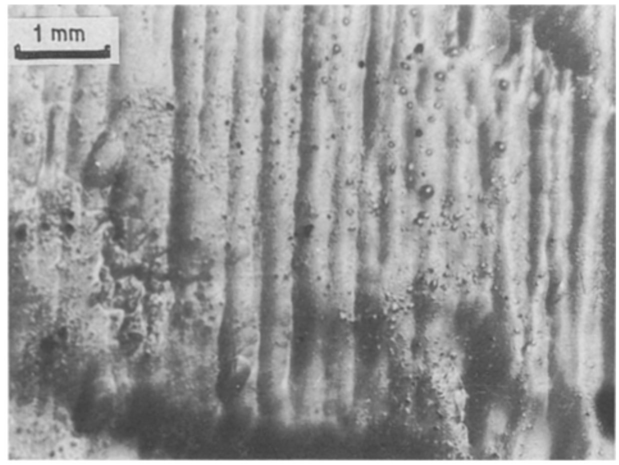


Figure 4 Typical etch channels on the (1 0 0) face of ADP formed after slight dissolution in water.

Fig. 2a were obtained after 20 s etching. It was observed that after re-polishing and re-etching the surface for 30 s some of the impurities disappear and a row of closely spaced pits resulting from an array of vertical edge dislocations appear, forming a low-angle tilt boundary, Fig. 2b. Re-polishing and re-etching the surface for 45 s and finally for 60 s shows no selective pits. The width of the tilt boundary has also been reduced due to annihilation of etch pits. Sometimes impurity clusters and precipitates produce etch pits on a crystal surface. Because these defects are localized at random in the crystal, etch pits due to them disappear continuously on prolonged etching (not shown).

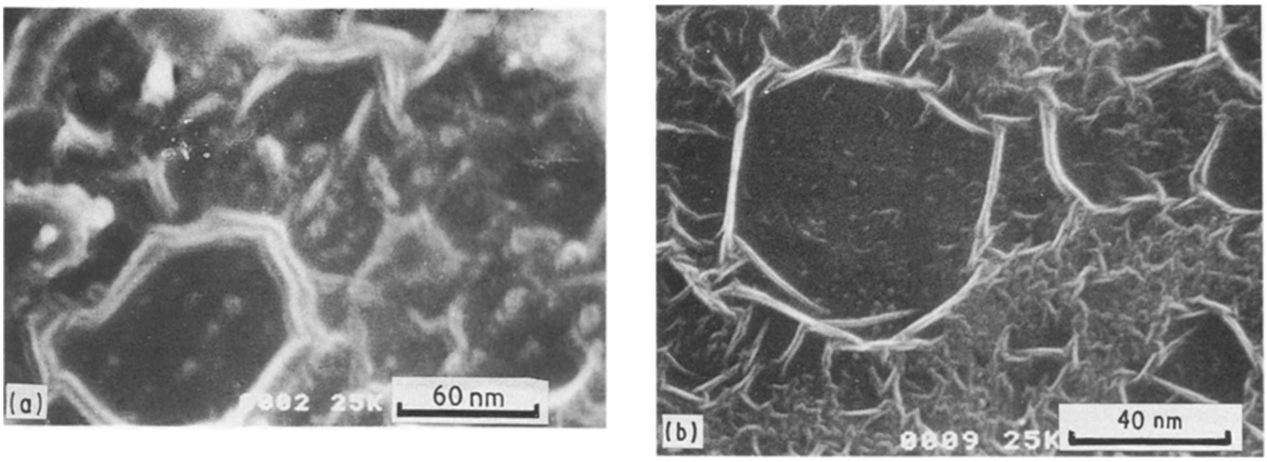
Etch pits of different morphologies were obtained after etching in KAP solution for different etch times. Parallelogram-shaped etch pits were observed after 20 s etching (Fig. 3a). Etch pits of different shapes were produced at the emergence point of dislocations after 30 s etching (Fig. 3b). Some growth striations perpendicular to the direction of growth were produced due to temperature fluctuations. A few hexagonal etch pits were obtained after re-polishing and re-etching the surface for 45 s and then finally for 60 s (Fig. 3c).

An interesting pattern was obtained after etching with doubly distilled water for 2 s. The lines shown in Fig. 4 are etch channels along [0 1 0] which correspond to stacking faults, i.e. misplaced (0 0 1) planes. Some etchants were also applied to the pyramidal (1 0 1) face, but no selective pits were observed. Scanning electron micrographs of the above etched faces were also taken (not all figures are shown). Fig. 5a–c show the pattern after etching with etchants 1, 2 and 3. Grain boundaries and low-angle boundaries were clearly observed.

4. Conclusion

The present etching study in gel-grown ADP crystals using different etchants has shown that each of the etchants used has its own specificity. The grain boundaries and stacking faults are only observed with the etchants H_3PO_4 and H_2O, respectively, but the behaviour of KAP is most interesting, which only shows hexagonal pits. Pits of different sizes observed on prism faces (1 0 0) reveal the presence of edge and screw dislocations in the crystal. It is also observed that etchants which reveal dislocations on prism faces do not necessarily reveal defects on pyramidal faces. The variation of etching time was found to be significant for etchants 1 and 2, but for KAP, etch time did not affect the morphology; prolonged etching leads to the disappearance of etch pits.

Therefore, it may be concluded that different etchants with varying etch times produce differences in the rates of dissolution at different dislocation sites,



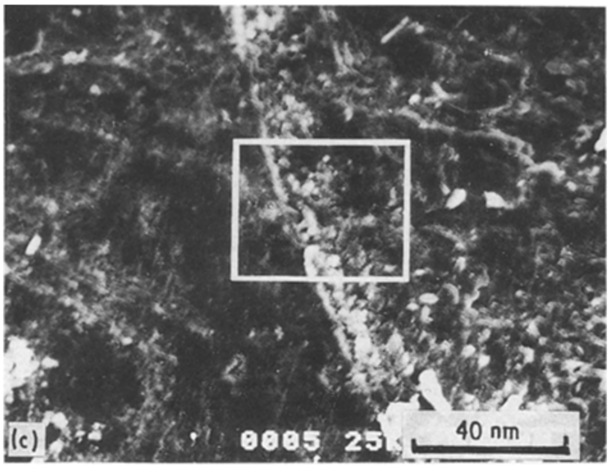


Figure 5 Scanning electron micrographs of the three etched faces.

which affect the undersaturation and thus change the pit morphology.

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