JOURNAL OF MATERIALS SCIENCE 20 (1985) 756–760

Tracking of dislocations in gel-grown gypsum single crystals

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Sparingly soluble calcium sulphate dihydrate (gypsum) crystals are grown by the gel method, derived from the diffusion of calcium chloride into the set gel containing ammonium sulphate. By etching (0 1 0) matched cleavages (of gypsum grown by above method) with analar grade nitric acid as well as successively etching a thin flake, it has been established that the tracks of dislocations initially make an inclination to the cleavage face and continue almost parallel to the cleavage face, contrary to the earlier findings on natural gypsum [1] where the dislocations are shown to be oblique, parallel lines passing through the body of the crystal. The change in the tracking of dislocations in gel-grown gypsum has been attributed to the role of gel inclusion, as well as a faster growth rate. The implications are discussed.

1. Introduction

The chemical etch method for studying the crystalline defects, has been well established as a simple technique for revealing the crystallographically oriented depressions called "etch pits". In producing well-defined etch pits, the selection of a suitable etchant is of paramount importance, for the ratio of the rate of dissolution along the cleavage face (V_l) to that normal to the cleavage along the dislocation (V_n), i.e. V_l/V_n, is at most 10 [2]. The sites at which etch pits nucleate have been shown to be the points of intersection of dislocations inside the crystal along the cleavage surface [3, 4]. The exact one-to-one correspondence between the etch pits and dislocations has been reported by several investigators, on etching both halves or cleavage specimens, as well as thin flakes (e.g. [5–9]). The nature and revelation of dislocations on etching matched rhombohedral and prism faces of synthetic quartz have been reported by Patel and Raju [10]. On etching matched faces of (0 1 0) basal cleavages of natural gypsum with nitric acid, evidence of edge and screw dislocations has been reported by Raju [11]. That the dislocations, in the act of cleavage are cut into smaller fragments and are oblique, parallel and continuous lines passing through the body of the crystal, has been shown by etching isolated, as well as matched pairs of (0 1 0) basal cleavages of natural gypsum [1].

It has been ascertained from (a) the chemical method, (b) the X-ray method, and (c) infrared spectroscopy [12], that the crystals grown in the gel medium are gypsum.

In the present paper, work carried out on tracking of dislocations on etching matched pairs and thin flakes along the (0 1 0) basal cleavage of gel-grown gypsum, is reported for the first time.

2. Experimental procedure

For the present work, gypsum single crystals were grown in sodium metasilicate gel, by imbedding before setting in 1 M ammonium sulphate and allowing 1 M calcium chloride to diffuse into the set gel. Details of the growth procedure have been reported by Raju [13]. The cleavages are obtained by inserting a razor blade parallel to the (0 1 0) plane and applying slight pressure, as in the case of natural gypsum. The matched pairs and thin flakes are etched in analar grade nitric acid and the etch patterns are studied by optical methods, as well as scanning electron microscope (JSM-35C), after coating the etched surface with a copper film (thickness 50 nm) to render the specimen conducting.

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Figure 1 Etch pattern on (0 1 0) face of gel grown gypsum; × 122.

3. Observations

Fig. 1 shows the typical etch pattern obtained after etching with nitric acid a (0 1 0) basal cleavage of gel-grown gypsum revealing (1) well defined rhombohedral etch pits, which are (2) asymmetric non-uniformly, and (3) point or flat bottomed, agreeing to a great extent with the reports on natural gypsum [7].

3.1. Etching of a matched pair

Instead of successively etching an isolated cleavage for different periods and then the matching faces, it was considered worthwhile to etch a matched pair, each face for different periods. Figs. 2a and b show the etch patterns produced on etching a matched pair with nitric acid, one face for 2 min and the other for 4 min.

The following points merit discussion:

1. the shape of the etch pits is the same on both faces;
2. one-to-one correspondence in the number and position of most of the pits exists on both faces, despite etching for different periods;
3. the size and depth of the pits increase with increase in the etching period; and
4. the arrays of pits do not correspond in size and depth (marked A and B in Fig. 2b).

3.2. Etching of a flake

Figs. 3a and b are the etch patterns in the same region of the opposite faces of a thin flake (150 μm thick) etched for the required period in nitric acid. It is surprising to see that one face (Fig. 3a) has a diagonal array of etch pits, while its opposite face (Fig. 3b) has vertical arrays of etch pits. It is apt to mention here, that on etching a flake (of 265 μm thick) of natural gypsum having (0 1 0) basal cleavage faces revealed a one-to-one correspondence between the etch pits on opposite faces [1], while a thinner flake (150 μm) of gel-grown gypsum, in the present case, shows no correspondence. In order to visualize the tracking of these etch pits, it was thought worthwhile to successively etch the flake for prolonged periods. Figs. 4a and b are the etch patterns of the same region, on etching the above flake for a prolonged period.

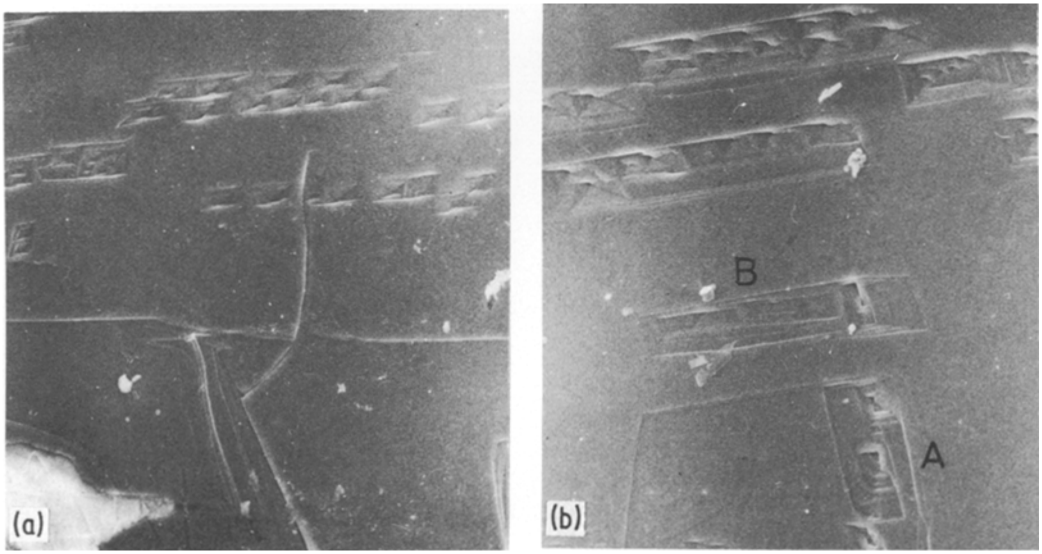

Figure 2 (a) and (b) Etch patterns on a matched pair; × 400.

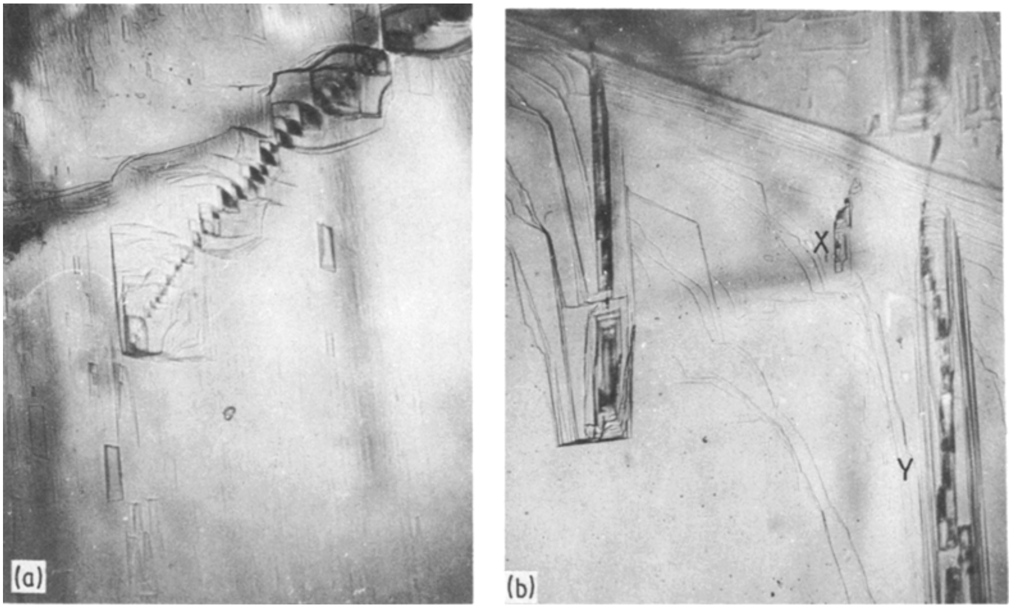

Figure 3 (a) and (b) Etch patterns on the opposite sides of a thin flake; × 280.

Attention is drawn to the following points:

1. when the diagonal array of pits is focused, an exact non correspondence exists with the vertical, parallel arrays of etch pits on the opposite face, seen as hazy vertical dark patches due to defocusing (see Fig. 3a) and vice versa;
2. the diagonal array of etch pits goes on diminishing in size and depth, on prolonged etching, and is finally observed to vanish, after very prolonged etching;
3. the short and long vertical arrays (marked X and Y in Fig. 3b) completely vanish on prolonged etching (cf. Figs. 3b and 4b). The dark diffuse patch representing the diagonal array of etch pits on its opposite face can be seen due to defocusing (Fig. 4b).

4. Discussion

The crystals grown in the gel medium, in the present case, reveal (0 1 0) basal cleavages and, on etching with nitric acid, well-defined rhombohedral etch pits are produced, agreeing well with earlier findings on natural gypsum [7] giving further evidence that the crystals are synthetic gypsum.

On etching each of the faces of the matched pair, in the same etchant, for different periods the size and depth increase with increase in etching time and a reasonable correlation in correspondence exists, suggesting that the sites at which etch pits are formed reveal the sites of intersection of a dislocation with the cleavage surface. During successive etching, as long as the asymmetric pits continue to enlarge in size and depth, it is indicated that the dislocations are proceeding obliquely to the cleavage surface in the crystal [7]. Deviation from a one-to-one correspondence in the etch patterns on the matched halves may occur due to branching of the dislocations in the cleavage plane. When branching occurs, a single pit before branching will then correspond to more than one pit, the number depending upon the number of branches the dislocation undergoes. In the present case, however, the corresponding etch pits constituting the arrays are either flat bottomed or vanishing (arrays marked A and B in Figs. 2a and b). Hence the deviation from correspondence may be attributed not to the branching of dislocations, but to their bending.

On prolonged etching the tail end of the diagonal array diminishes in depth (cf. Figs. 3a and 4a); this can be explained as being due to bending of dislocations nearly parallel to the cleavage, in which case V_n decreases, as observed. The only possible explanation for the shrinking of the diagonal array of etch pits (Figs. 3a and 4a) and the vanishing of vertical arrays of etch pits (X and Y in Fig. 3b) may be given by the schematic diagram shown in Fig. 5. PQ and RS are the upper and lower faces of the flake during the first stage of etching, while after prolonged etching, EF and GH

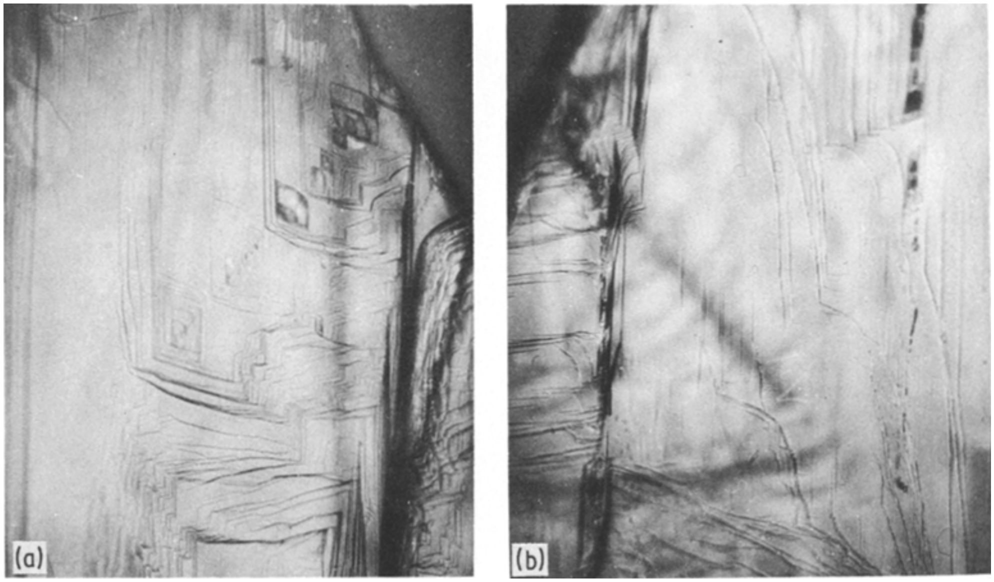

Figure 4 (a) and (b) Regions of Figs. 3a and b after prolonged etching; × 280.

are the upper and lower faces. The continuous lines are the dislocation tracks meeting the upper face while broken lines are on the lower face. The dislocation lines meeting the cleavage face are marked by solid dots which represent dislocation etch pits. The array of etch pits on the upper face PQ (say diagonal array) consisting of ten etch pits in Fig. 5 (hypothetically), shrinks to an array of five pits on prolonged etching. Similarly, the dislocation arrays X and Y on the lower face RS vanish completely, because the crystal will have dissolved as far as GH, on prolonged etching (as seen in Fig. 5). Thus the probable tracks of dislocations are initially inclined to the cleavage and then proceed parallel to it, thus explaining the deviation from correspondence on matching faces as well as thin flakes.

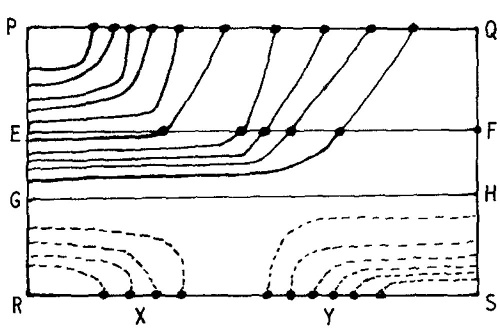

Figure 5 Schematic diagram to show dislocation tracks.

5. Conclusions

The well-defined asymmetric pits traceable on etching matched faces, which enlarge in size and depth on successive etching, suggest that the dislocations are inclined towards the cleavage surface [7]. Decrease in number and the vanishing of etch pits in the arrays on prolonged etching of the flake, gives a strong indication that the tracks of dislocations are initially inclined towards the cleavage, and then proceed almost parallel to the cleavage face, as shown schematically in Fig. 5.

The dislocations in natural gypsum have been reported to be linear, inclined and parallel [1], while in the present case of gel-grown gypsum, the dislocations are shown to be initially inclined, becoming curved and thereafter deviating almost parallel to the cleavage plane. The probable explanation for this may be as follows: the natural crystals take years to grow, and the growth parameters (temperature and pressure) do not change abruptly, rather very gradually according to climatic conditions. In the case of gel-grown gypsum, growth is rapid (3 to 4 weeks) and gel particles become embedded, giving rise to different morphologies as reported by Jayakumar and Raju [14]. The X-ray energy dispersive spectrum of the gel-grown gypsum, which gives evidence of the presence of SiO_2 by weight, absent in the natural crystal, will be published elsewhere. Hence the gel particles which are trapped in the growing crystal may release stresses to the growing crystal in the gel medium, which in turn, induce the curved dislocation path, as established in the present investigations.

Acknowledgements

The author wishes to thank Professor Dr J. Heydenreich, Institute for Solid State Physics and Electron Microscopy, Academy of Sciences of German Democratic Republic, Halle 4020 (DDR) for his continued encouragement and in whose Institute this work was carried out. The sponsorship by the Madras University authorities and the University Grants Commission, New Delhi in the Cultural Exchange Programme between Indo-German Democratic Republic is highly appreciated.

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Received 28 February and accepted 10 April 1984