PART II
## CHAPTER 4

**ETCHING OF NATURAL SrSO₄ CRYSTAL CLEAVAGES**

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4.1 Introduction

When crystals are subjected to dissolution in some etchants under suitable conditions, small geometrical depressions called the 'etch pits' appear on their surfaces. As the shape of these etch pits is intimately associated with the internal structure of the crystal a study of their shape can assist one in determining the symmetry of the faces on which they occur and hence that of the crystal. However, the shape of the etch pits on a crystal face also depends on the choice of the etchant.

Etching technique has also been proved to be a powerful tool in locating the dislocation sites emerging on the crystal surfaces. A perfectly cleavable crystal
provides fresh surfaces for such a study and hence can conveniently be used to make a detailed study of imperfections in them. For such a study it is essential to look for a suitable etchant. As there exists no hard and fast rule for the selection of an etchant one has to resort to trial and error method to find them. Several workers have produced etch pits on crystal cleavages which they believed were located at dislocation sites and have studied dislocations in detail.

It is evident that a comparative study of synthetic and natural crystals with reference to their quality can very easily be facilitated if one has the knowledge of distribution, configuration, structure, density etc. of dislocations in natural crystals at hand. It is this idea that led the author to investigate these aspects in natural SrSO₄ crystals as the subsequent chapters mainly deal with the study of the growth of barite group crystals and the imperfections in them with special reference to SrSO₄. Naturally the etching method was employed. The investigations thus carried out are presented in this chapter. Celestite crystals from the following localities have been used for the work reported here. (i) Yate area, Bristol, England, (ii) Strontian Island, Lake Erie, U.S.A. (iii) Virginia,
4.2 Crystal Cleavage

As mentioned in chapter 1, SrSO₄ crystal has perfect ((001)) and nearly perfect ((210)) cleavages. While cleaving the crystal, it was observed that ((001)) cleavages could be obtained very easily by just pressing the sharp edge of a blade along ((001)). On the contrary, to cleave the crystal parallel to ((210)) a blow to the blade was always necessary. The greater ease of ((001)) cleavage as compared to ((210)) cleavage suggests that the binding energy between the atoms in the two neighbouring (001) planes may be less than that between the atoms in the two neighbouring (210) planes.

Both the cleavages produced as mentioned above were examined optically as well as by multiple beam interferometry. The figs. 4.1(a) and 4.2(a) respectively show the general characteristics of (001) and (210) cleavages. The topography of both these faces is revealed by the multiple beam interferograms shown in figs. 4.1(b) and 4.2(b).

4.3 Etching of ((001)) Cleavage Faces.

With a view to revealing dislocation sites on
several etchants were tried. From a large number of experiments it was found that conc. H$_3$PO$_4$ at a temperature of 120°C (or more up to 240°C) could produce well defined observable etch figures in about 30 minutes. Following experiments were conducted to establish its fidelity in revealing the dislocation sites.

4.3.1 Successive etching

A freshly cleaved (001) face was successively etched for two different periods. Figures 4.3(a) and 4.3(b) thus represent respectively the etch patterns produced after 30 minutes and 50 minutes each, from which we can infer that the individual pits grow bigger in size with time but their number remains the same.

4.3.2 Etching of matched cleavages

Figures 4.4(a) and 4.4(b) show typical etch patterns on the two exactly opposite matched faces etched simultaneously for about 40 minutes. One can easily note that there exists a perfect matching in the number and positions of etch pits on the two faces.

4.3.3 Etching of opposite sides of a thin flake

In order to see whether there exists correspondence of etch pits on the two sides of a thin flake, a thin
flake was selected and etched. Figures 4.5(a) and 4.5(b) show the etch patterns on the two opposite sides of a flake of ~300 μm thick, fig. 4.5(c) being the transmission photograph showing both the faces. As expected a perfect correlation of etch pits exists.

4.3.4 Etching of an indented cleavage face

When an indented cleavage was etched in the said etchant for a required period rosette patterns were produced around the indentation marks. A typical rosette pattern thus produced is shown in fig. 4.6.

4.3.5 Etching of heated cleavages

The etching of heated cleavages also revealed that the pits behave as would be expected if they were associated with dislocations. For example, they were found to move upon heating as is evident from below.

A crystal cleavage was first etched to get etch pits and then it was heated at 900°C for about 2 hrs. After cooling it slowly down to room temperature the cleavage face was again etched. The pattern produced in this way is shown in fig. 4.7. Obviously, we observe that several pits have been displaced from their initial positions, the initial positions being represented by the flat bottomed pits. Further when a cleavage, which
was heated to the same temperature and then quenched, was etched, pairs of pits were produced on it. The above observations could be explained only if the pits are associated with dislocations, the pairs of pits produced in the latter case being caused due to the production of dislocation half loops during quenching.

From all the above observations one can definitely conclude that conc. H₃PO₄ etchant is capable of revealing both the grown-in and fresh dislocations in the crystals.

4.3.6 Dislocation configuration

To obtain some information regarding the geometrical configuration of dislocations the structure of some selected pits were studied critically. Thus figs. 4.8(a) and 4.8(b) represent a pair of matched cleavages selected for such a study, etched in conc. H₃PO₄ under identical conditions. It may be noted that majority of the pits in figs. 4.8(a) and 4.8(b) are eccentric. Moreover, some of the pits are displaced with respect to their corresponding pits on the counterpart (see pits marked a, b, c, d and a', b', c', d'). Obviously, the eccentricity and the displacements of the pits can be attributed to the inclined nature of dislocation lines. Further, one can also
see from the photographs that there exists some discrepancy in the number of pits. For example, the pits marked A and B in fig. 4.8(a) have three pits each on their counterpart (regions marked A' and B') the magnified pictures of which are shown in figs. 4.8(c) and 4.8(d). Such discrepancies can easily be explained on the basis of bending and branching of dislocations as reported by Sagar and Faust. \(^1\)

Figure 4.9 represents an etch pattern which reveals the existence of dislocation loops in the body of the crystal. It may be noted from the figure that the bottoms of the paired pits have almost coalesced. On further etching they turned out to be a single flat bottomed pit and finally disappeared.

Many a time together with point bottomed pits, flat bottomed pits were seen and on prolonged etching of the same face these used to grow larger developing new small point bottomed pits within their periphery, as seen in fig. 4.10. This process of generation of new pits within the old ones may be due to the existence of stepped dislocations in the crystal.

4.3.7 Variation of density of pits

The density of etch pits on \(((001))\) cleavages of natural crystals varies between wide limits. Often a
sudden change in pit density as seen in fig. 4.11 was observed which may be due to the sudden fluctuations in the growth conditions. The average pit density also was different for crystals from different localities, as shown in table No. 4.1 which may again be attributed to different growth conditions and environment in which they have grown.

4.4 **Etching of \((210)\) Cleavages**

The above etchant which could reveal dislocation sites on \((001)\) cleavage faces also produced well-defined etch pits on \((210)\) cleavages under the same conditions. All the experiments mentioned in section 4.3 to establish the suitability of the etchant to reveal dislocation sites, when conducted on \((210)\) cleavages proved beyond doubt that the pits produced by this etchant on this cleavage are dislocation pits. In figs. 4.12(a) and 4.12(b) we can see one-to-one correspondence of etch pits between the \((210)\) matched cleavages which is one of the commonest observations displayed to prove the capability of an etchant to reveal dislocations.

The establishment of a dislocation etchant which could reveal dislocation sites on both the cleavages has enabled the author to reveal some structural defects present
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Locality</th>
<th>Colour</th>
<th>Maximum size</th>
<th>Dislocation density (pits/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Yate area, Bristol, England.</td>
<td>Bluish</td>
<td>2.5 x 1.7 x 1.0 cm³</td>
<td>2.4 x 10⁵</td>
</tr>
<tr>
<td>2.</td>
<td>Strontian Island, Lake Erie, U.S.A.</td>
<td>Translucent slightly milky</td>
<td>5.5 x 4.0 x 1.5 cm³</td>
<td>7.1 x 10⁴</td>
</tr>
<tr>
<td>3.</td>
<td>Virginia, (East Stone Gap), U.S.A.</td>
<td>Bluish tinge sky blue</td>
<td>1.0 x 0.5 x 0.5 cm³</td>
<td>1.1 x 10⁵</td>
</tr>
<tr>
<td>4.</td>
<td>Texas, (Lampasas), U.S.A.</td>
<td>Slightly milky</td>
<td>2.0 x 1.0 x 1.0 cm³</td>
<td>3.0 x 10⁵</td>
</tr>
<tr>
<td>5.</td>
<td>Vassev, Haute Marne, France.</td>
<td>Transparent</td>
<td>0.3 x 0.2 x 0.1 cm³</td>
<td>2.1 x 10⁵</td>
</tr>
<tr>
<td>6.</td>
<td>Girgenti, Sicily, Italy.</td>
<td>Transparent</td>
<td>0.4 x 0.1 x 0.1 cm³</td>
<td>1.0 x 10⁶</td>
</tr>
</tbody>
</table>
in these crystals. These have been briefly described below.

4.5 Polygonization

Several features characteristic of polygonization have been observed on (001) cleavage faces due to etching. A typical instance of polygonal walls lying in \([100]\) is shown in fig. 4.13. It can be noted from the figure that the walls are not as straight as glide bands and are discontinuous. Figure 4.14 reveals polygonization along \([010]\).

4.6 Grain Boundaries

Microscopic as well as diffraction studies have revealed that real crystals (unlike ideal crystals in which the lattice planes are supposed to have same orientation) are composed of small blocks or grains with slightly different orientations giving rise to what are called grain boundaries. The fact that such grain boundaries can very well be revealed by the technique of dislocation etching was first verified by Vogel et al. They have shown in germanium that the spacing of etch pits in grain boundaries corresponds to the predicted value based on the theoretical model of Buerger and Bragg (Refer fig. 4.15).

Etching of natural \(\text{SrSO}_4\) cleavages often
revealed closely spaced etch pits arranged in rows representing grain boundaries. Figure 4.16 is a high magnification picture (electron micrograph) of a linear grain boundary observed on a (001) cleavage face after etching. One can appreciate the regularity of spacings between the etch pits. Figures 4.17(a) and 4.17(b) are etch patterns on two matched (001) cleavages in which matching of grain boundary is seen. Further, typical etch patterns illustrating the intersection of grain boundaries are shown in figs. 4.18 and 4.19.

Grain boundaries have also been observed on (210) cleavages. An example of this is shown in fig. 4.20.

4.7 Inclusions

Crystals growing from solution often trap mother liquor in the form of shallow veils parallel to a growth face and these are called inclusions. Usually the cavities enclosing the inclusions are of different size and are distributed in a haphazard manner in the crystal, but often they are approximately equiaxial and are arranged in a preferential fashion. The formation of inclusions depends upon a large number of growth parameters such as temperature fluctuations, local concentrations, crystal size, composition of the parent solution, growth rate etc.
Inclusions which may be solid, liquid or gaseous often play an important role in determining the strength of the crystals. Henderson\textsuperscript{5} has reported that large incoherent precipitates act as dislocation sources in MgO and consequently lead to a low yield stress. Gross\textsuperscript{6} has observed liquid inclusions in RDX crystals trapped at dislocation sites.

One of the major defects in natural SrSO\textsubscript{4} crystals is the inclusions. When cleavages of these crystals were examined under microscope without silvering a continuous distribution of tiny isolated (and less often large) inclusions were observed on and just below the cleavage faces. One such case is shown in fig. 4.21. By racking down the microscope one could visualise the distribution of these inclusions in the interior part of the crystal.

Crystal surfaces containing large inclusions when etched used to give clusters of etch pits around the inclusions. Figure 4.22 illustrates one such case. At times, etching of natural SrSO\textsubscript{4} cleavages instead of clusters of etch pits, used to reveal regular rosette-like patterns around inclusions, representing volume indentation, as shown in fig. 4.23. In this figure the arms of the rosette
are along \([100]\). From these observations the author is inclined to believe that the large inclusions present in the crystal act as dislocation sources and the generation of such dislocation clusters, which are probably in the form of loops, might have occurred due to the slip which would release the thermal stresses arising due to the differential thermal contraction of the parent crystals and the material enclosed.

So far as the composition of these inclusions is concerned nothing can be spoken definitely at present. However, it appears that the solid inclusions are perhaps more effective in generating dislocations.

4.8 Conclusions

1. Conc. \(\text{H}_3\text{PO}_4\) works as a dislocation etchant for both \((001)\) and \((210)\) cleavages of natural \(\text{SrSO}_4\) crystals.

2. Natural crystals of \(\text{SrSO}_4\) contain large number of structural defects common to all plastically deformable crystals.

3. The dislocation density of \(\text{SrSO}_4\) crystals obtained from various localities ranges between \(10^4/\text{cm}^2\) and \(10^6/\text{cm}^2\).

4. Large inclusions, probably solid are found to
act as dislocation sources.

5. Dislocations in natural SrSO$_4$ crystals are often branched, bent or inclined.

References


