PART III
CHAPTER 6

GROWTH OF STRONTIUM SULPHATE SINGLE CRYSTALS BY THE CHEMICALLY REACTED FLUX METHOD AND THEIR DISLOCATION CONFIGURATION

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6.1 **Introduction**

The fact that the barite group crystals are highly insoluble in water and decompose on or before melting, naturally prevents them from being grown by the conventional methods, such as 'growth from aqueous solution', 'melt growth' or 'growth from vapour phase'. Consequently, even though the precipitation kinetics and the mechanism of formation of these crystals have been extensively studied\(^1-4\) over the past few years, only a very few attempts have been made to grow them in the laboratory. Until recently, the largest crystals of these grown in the laboratory scarcely exceeded microscopical size.
On the contrary, the nature has been far more successful in building up large crystals of barite, celestite and anglesite. Crystals of several centimeters in length are very common in nature, of course, with obvious limitations in their perfection and purity. These facts naturally stimulate experimentalists to try to synthesise them in the laboratory with the commoner substances at their disposal by some suitable method.

As a result of the continued efforts that were being made in our laboratory for the last few years in this direction, Patel and Koshy\textsuperscript{5}) could synthesise barium sulphate crystals (barite) of appreciable size employing the chemically reacted flux method. This method, first reported by Schieber\textsuperscript{6,7}), involves the chemical reaction between the constituents of a stoichiometric mixture in the molten phase to form the desired product and its subsequent crystallisation at a temperature considerably below the melting point of the crystal to be grown. Following the same procedure the author has grown single crystals of strontium sulphate (celestite) and this chapter deals with their growth, morphological studies and the dislocation configuration. The studies on dislocations were made by the usual etch pit method.
6.2 Growth Technique

By the double decomposition of strontium chloride and sodium sulphate, the production of strontium sulphate can be materialised according to the following equation.

\[ \text{SrCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{SrSO}_4 \downarrow + 2\text{NaCl} \]

To carry out the reaction in the molten state, a stoichiometric mixture of analytical grade \( \text{SrCl}_2 \) and \( \text{Na}_2\text{SO}_4 \) taken in a platinum crucible was heated in a muffle furnace at 950°C which is well above the melting points of both the constituents. The melt was kept at that temperature for about 6 hours and then the temperature was gradually brought down to room temperature at a uniform rate in about 24 hours. Single crystals of strontium sulphate which are insoluble in water were separated by immersing the solidified material in water which dissolved NaCl leaving behind the crystals of strontium sulphate. An appreciable increase in the size of the crystals was observed by keeping the melt at 950°C for a longer duration. Figure 6.1 shows some typical crystals grown by this method. With the help of X-ray rotation photograph (fig. 6.2) the crystals were identified to be \( \text{SrSO}_4 \). The calculated lattice constant
(a = 8.38 \AA; b = 5.39 \AA \text{ and } c = 6.82 \AA) \text{ were found to agree with those reported for strontium sulphate.}

6.3 Morphology of Crystals

It is seen from fig. 6.1 that the crystals grown are of appreciable size, some of them being about 5 mm long and 2 mm broad. Almost all the crystals were bounded by ((011)) and ((101)) faces. Figure 6.3 shows the typical microstructures consisting of dendritic patterns on the habit faces. It may be mentioned that such dendritic patterns were observed invariably on all the habit faces of the crystals grown by this method and were generally non-crystallographic in nature.

The crystals were cleaved along ((001)) and ((210)) and it was observed that the cleavages thus produced were similar to those obtained in natural crystals. The cleavages were distinguished one from the other with the help of Laue photographs. While ((001)) cleavages exhibited a perfect two-fold rotational symmetry (fig. 6.4), characteristic of an orthorhombic system ((210)) cleavages showed no such symmetry (fig. 6.5). Figure 6.6(a) shows a typical (001) cleavage while fig. 6.6(b) presents an interferogram over this cleavage face showing the topography of it. It is evident from the
The hardness of these crystals determined by indenting the cleavage faces with Vickers microhardness indentor was found to lie between 3.1 and 3.2 in Mohs' scale, which is in the range of the hardness of the natural crystals. It was thus confirmed that the chemically reacted flux gave single crystals of strontium sulphate having the same characteristics as that of natural crystals.

6.4 Etching

To study the dislocation content and their configuration the synthetic crystals were etched in a suitable etchant. Naturally conc. \( \text{H}_3\text{PO}_4 \), the dislocation etchant of natural \( \text{SrSO}_4 \) crystals, was tried first. Even though this etchant gave good etch pits on the habit faces of synthetic crystals it could not work well with the cleavage faces. Hence efforts were made to modify this etchant so that it could etch both the habit as well as cleavage faces equally well. After some trials it was found that conc. \( \text{H}_3\text{PO}_4 \) containing \( \sim 0.5 \text{ mg/ml of MgO} \) could give well defined pits both on habit and cleavage faces at about 120°C in about 2 hours. The geometrical shape of the etch pits was related to the crystallographic...
faces on which they occurred. Two types of pits were in common.

1. Triangular pits. These occurred on (011) habit faces (fig. 6.7).

2. Four-sided pits which occurred on (101) habit faces as shown in fig. 6.8.

On habit faces, sometimes, rows of etch pits were also observed.

The shape of the etch pits on (001) cleavage faces is similar to those observed on (001) cleavages of natural crystals. A typical example of the etch patterns produced on (001) cleavages of synthetic crystals by the modified etchant is shown in fig. 6.9.

6.5 Correspondence of Etch Pits and Dislocations

It is evident from the following observations that the etch pits thus produced nucleate at the sites of dislocations on the crystal surfaces.

1. The pits can be followed progressively into the crystals during successive etching.

2. There is a perfect matching in the number and position of etch pits on the matched cleavages as seen in figs. 6.10(a) and 6.10(b).
3. One-to-one correspondence of etch pits on the opposite faces of thin flakes is also observed.
4. The indented cleavages when etched revealed rosette patterns around the indentations.

The above mentioned etchant could also etch \((210)\) cleavages of synthetic SrSO\(_4\) crystals preferentially at dislocation sites. Figures 6.11(a) and 6.11(b) reveal a perfect matching of etch pits produced on \((210)\) matched cleavages.

It should be noted here that the addition of MgO to conc. H\(_3\)PO\(_4\) does not alter its effectiveness in revealing dislocation sites on natural SrSO\(_4\) crystal cleavages. Both the original and the modified etchants work equally well so far as the natural crystals are concerned.

6.6 Inclined Dislocations

In order to study the configuration of dislocations within the body of the crystal, a thin flake was selected and etched. One-to-one correspondence in number and position of pits produced on its two sides was observed. The plate was further cleaved along \((001)\) producing four thin flakes. All the thin flakes were then simultaneously etched in the said etchant under suitable
conditions. It was indeed interesting to note that in the corresponding regions the etch pits formed the same patterns on all the faces. It was also observed that (i) the sizes of the pits differed and (ii) the etch patterns on the two sides of a thin flake showed a remarkable shift. While comparing the sizes of the pits on different faces it was observed that there existed correlation even regarding the sizes of the pits in the corresponding regions. Out of several pits having one-to-one correspondence on all the faces, some four were selected from the three thin flakes I, II and III and their corresponding shifts were measured for each flake. The thickness of the flakes in the vicinity of the concerned pits were also measured. Thus the inclinations of dislocation lines were calculated and are given in table No. 6.1.

It may be noted from this table that:

1. The dislocation lines have different inclinations.
2. Inclination of a particular dislocation line remains the same in all the three flakes within the limits of the experimental error.

During the course of the above investigations a measurement of dislocation density over a large number of cleavage faces was also made. The dislocation density varied from \(10^3/\text{cm}^2\) to \(10^4/\text{cm}^2\).
### Table No. 6.1

<table>
<thead>
<tr>
<th>Flake No.</th>
<th>Pit No.</th>
<th>Shift 's' in μm</th>
<th>Thickness 't' in μm</th>
<th>Inclination θ: $θ = \tan^{-1} (t/s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.</td>
<td>67.42</td>
<td>90</td>
<td>53° 10'</td>
</tr>
<tr>
<td>I</td>
<td>2.</td>
<td>52.57</td>
<td>92</td>
<td>60° 15'</td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>50.27</td>
<td>89</td>
<td>60° 31'</td>
</tr>
<tr>
<td></td>
<td>4.</td>
<td>40.86</td>
<td>106</td>
<td>68° 55'</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>1.</td>
<td>92.00</td>
<td>121</td>
<td>52° 45'</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>80.00</td>
<td>141</td>
<td>60° 32'</td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>80.00</td>
<td>140</td>
<td>60° 15'</td>
</tr>
<tr>
<td></td>
<td>4.</td>
<td>63.14</td>
<td>160</td>
<td>68° 35'</td>
</tr>
<tr>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>III</td>
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<td>82.14</td>
<td>112</td>
<td>53° 46'</td>
</tr>
<tr>
<td></td>
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<td>59° 36'</td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>66.28</td>
<td>114</td>
<td>59° 49'</td>
</tr>
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<td></td>
<td>4.</td>
<td></td>
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</tbody>
</table>
6.7 Discussion

Strontium sulphate is formed due to the double decomposition of Na$_2$SO$_4$ (M.P. 884°C) and SrCl$_2$ (M.P. 873°C) in the molten state. As the melting point of SrSO$_4$ (M.P. 1580°C) is higher than the melting point of NaCl (M.P. 801°C), due to reaction, SrSO$_4$ may precipitate slowly and this forms single crystals when the melt is cooled leaving behind the NaCl melt which will subsequently solidify. The nature of the dendritic patterns which are invariably observed on all the crystals suggests that at the end of the growth due to supercooling dendritic deposition takes place on the crystal faces.

The individual isolated pits reveal the sites of dislocations as in the case of other mineral crystals. The rows of pits observed on the habit faces indicate that the dislocations might have re-arranged themselves to get polygonised during the crystallisation and subsequent cooling process.

The observations made on the inclination of dislocations using the thin flakes show that the majority of dislocation lines run straight through the body of the crystal with different inclinations. This difference in inclination of dislocations itself might be responsible for
the difference in the size of the individual pits. In fact from the author's observations it was found that larger the inclination the smaller was the size of the pits. However, an exact relation between the inclination and the rate of dissolution has not been worked out.

The low dislocation density of the synthetic crystals establishes the usefulness of this method of growth in getting crystals of a better quality.

6.8 Conclusions

1. Single crystals of SrSO₄ have been grown by the chemically reacted flux method.

2. The crystals are usually bounded by (011) and (101) habit faces.

3. Dendritic deposition seems to occur during the last stage of the growth.

4. Conc. H₃PO₄ containing ~0.5 mg/ml. of MgO could etch both the habit as well as cleavage faces equally well at about 120° C.

5. Majority of dislocation lines run straight through the body of the crystals.

6. Inclinations of dislocations seem to influence the rate of dissolution at dislocation sites.
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