CHAPTER 10

GROWTH OF SINGLE CRYSTALS OF BaSO₄ AND SrSO₄ FROM GELS

CONTENTS

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>10.2</td>
<td>Crystal Growth Technique</td>
</tr>
<tr>
<td>10.3</td>
<td>Crystal Morphology</td>
</tr>
<tr>
<td>10.4</td>
<td>Discussion</td>
</tr>
<tr>
<td>10.5</td>
<td>Conclusions</td>
</tr>
</tbody>
</table>

References 127
10.1 **Introduction**

Procedures for growing crystals in gels have been known since the end of the last century, but the method had fallen largely into oblivion until, a few years ago, the interest in it was stimulated afresh by the need for a variety of crystals which could not be grown by conventional techniques. Since then various modifications of the gel method have been suggested by and used to grow different types of crystals with a high degree of perfection and more informations have been obtained on the mechanism of growth as well as on the factors that control nucleation. In this method since the two soluble reactants are allowed to diffuse through the gel and react to form
an insoluble product it is obviously suitable for growing only those crystals which have very low solubility in water. Nonetheless by virtue of its unusual combination of low temperature growth with exceedingly simple and inexpensive equipment, the gel growth technique offers an attractive alternate method for growing this restricted class of crystals viz. insoluble crystals.

Crystals do grow in a variety of gels, but for practical purpose the growth media which are of concern are silica gels. In the usual procedure one reagent is incorporated in the gelling mixture taken in a simple test tube and another is later diffused into the gel leading to a very high supersaturation and in due course, to nucleation and crystal growth. Alternatively, a U tube may be used with the gel at the bottom and the reactants added to the arms of the tube. This is of course growth from solution, but differs from the conventional procedures by the absence of convection currents. The gel medium prevents turbulence and remaining chemically inert, provides a three-dimensional structure which permits the reagents to diffuse at a desirable controlled rate. Further, its softness and the uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth even in the
presence of impurities. The other chief merits of this technique are

1. The crystals can be observed practically in all stages of growth.

2. Since the crystals grow at low temperature they contain quite a lower concentration of equilibrium defects than those grown by high temperature techniques.

3. The crystals are separated spatially and hence the effects, if any, due to the precipitate-precipitate interactions are prevented.

Obviously, barite group crystals are well suited for the gel growth technique by virtue of their high insolubility in water. Even though crystals of a large number of substances including metals such as gold$^{10)}$ and lead$^{11)}$ have been grown by this method, it seems, no successful effort has been made to grow these crystals. Hence it was thought worthwhile to make an attempt to grow these crystals as this facilitates a comparative study of them with those grown from flux. The work presented in this chapter is restricted to the growth of single crystals of BaSO$_4$ and SrSO$_4$ and their morphological studies.
10.2 Crystal Growth Technique

Eventhough the basic principle involved in the present growth experiments is the same as that of Henisch et al.\textsuperscript{1)} the author has slightly modified the experimental design so as to grow bigger crystals. During preliminary experiments tubes of 1 - 2 cm diameters were employed to grow these crystals. Only tiny crystals of about less than half a millimeter in dimension grew at the gel feed solution interface, and just below it. Bloor\textsuperscript{12)} while growing rare earth double sulphates in gels, has observed that the crystals formed in larger tubes were generally larger than those formed in the smaller ones and he has attributed this to the greater lateral diffusion to growth sites which could be possible only in larger tubes. In view of this it was considered to provide greater freedom for lateral diffusion of ions by some modifications of the conventional apparatus. The apparatus used for growing crystals of BaSO\textsubscript{4} and SrSO\textsubscript{4} by using gel are schematically shown in figs.10.1(a) and 10.1(b). 100 ml of sodium silicate solution of specific gravity 1.05 or less was taken in a beaker to which the required quantity of 2N hydrochloric acid was added to form gel. Before the gel was set a glass tube of 1 - 2 cm diameter was inserted as shown in
fig. 10.1(a). In the apparatus shown in fig. 10.1(b) instead of inserting one glass tube two identical glass tubes were inserted. The time taken for the gel to set varied from a couple of minutes to several days depending upon the concentration and pH value of the solution. After the setting of the gel the growth experiments were started by adding the feed solutions. The growth experiments were carried out at desired temperatures using a constant temperature water bath controlled by a toluene regulator.

The chemicals used for growing the crystals were (i) B.D.H. 'Analar' SrCl₂ (ii) B.D.H. 'Analar' BaCl₂ and (iii) B.D.H. 'Analar' Na₂SO₄. The following reactions were employed for the formation of single crystals of BaSO₄ and SrSO₄:

\[
\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + 2 \text{NaCl}
\]

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

For growing BaSO₄, 0.2N solution of BaCl₂ was poured into the beaker while 0.2N solution of Na₂SO₄ was poured into the tube in the case of apparatus shown in fig. 10.1(a). In the case of apparatus shown in fig. 10.1(b), one tube was filled with BaCl₂ solution and the other with the Na₂SO₄ solution, and some distilled water was poured
into the beaker above the gel to keep the gel wet so that it may not break. SrSO$_4$ was grown by exactly the same method taking SrCl$_2$ instead of BaCl$_2$.

The apparatus, basically functioning in the same manner as the U tube, have the advantage of providing greater freedom for lateral diffusion. They are simple and can be easily cleaned. Henisch et al. have suggested that the increasing presence of reaction waste products gradually diminishes the rate at which the new materials can reach the growing crystal surfaces. The apparatus shown in fig. 10.1(b) can be employed to avoid this to some extent because the reaction waste products can diffuse towards water above the gel and hence decrease the concentration of the reaction waste products around the crystals that are growing.

10.3 Crystal Morphology

Single crystals of BaSO$_4$ and SrSO$_4$ started growing in the gel near the mouth of the tubes a few days after the feed solutions were added and grew up to 1 - 2 mm in length in about four weeks. Figures 10.2 and 10.3 show some typical crystals of BaSO$_4$ and SrSO$_4$ respectively grown in the laboratory by the above method. It is seen in the photomicrographs that the
smaller crystals are more transparent and well defined, while the larger ones appear to be not so well defined implying thereby that the crystal quality decreases with the increase in size in these cases. The progressive deterioration in the crystal quality was also confirmed by obtaining X-ray diffraction photographs. The smaller transparent crystals gave sharp diffraction spots in the X-ray rotation photographs whereas the larger ones gave extended spots. In addition to this, the X-ray rotation photograph of larger crystals gave faint powder lines. The appearance of these lines may be due to the large number of multioriented tiny platelet crystals grown on the surface of the parent crystal during the later stages of growth as can be clearly seen in fig. 10.4. However, small crystals were devoid of these multioriented platelet structures. It was observed that BaSO₄ also behaved in the same manner.

The morphology of both BaSO₄ and SrSO₄ single crystals grown under similar conditions was the same. The change in the concentration of the feed solution had no effect on the morphology of the crystals grown. Gel pH also was not found to be a significant factor in deciding the size and morphology of the crystals eventhough better crystals were formed when the gel pH was between
6 and 9. However, it was observed that there was a considerable effect of the growth temperature on their morphology. For example, in the case of SrSO$_4$, all the crystals grown at about 35°C had \((011)\) and \((101)\) as their habit faces whereas the crystals grown at about 20°C developed \((001)\) habit faces in addition to the usual \((011)\) and \((101)\) faces. Several crystals exhibiting interpenetrating twinning had also been observed in this case. Figure 10.5 shows some of the crystals of SrSO$_4$ grown at about 20°C. One can easily identify the crystals (marked A) having additional \((001)\) habit faces in the figure.

10.4 Discussion

It is evident that in silica gel the growing crystals either displace$^{13}$ or trap the gel$^{14}$ as they grow. In the case of displacing of the gel cusps can be seen round the crystal, while in the other case since the crystals incorporate the gel as they grow, the final crystals look turbid. From the appearance of BaSO$_4$ and SrSO$_4$ crystals that have been grown in gels, it seems that they incorporate gel as they grow and hence become transluscent. The incorporation of gel in the crystals was further confirmed by dissolving the crystals in nitric
acid which left the skeleton of silica gel behind. In addition, the progressive deterioration of crystal quality indicates an increasing incorporation of gel with time as observed by Bloor\textsuperscript{12}) in the case of rare-earth double sulphates. This might probably be responsible for the deformation of the faces observed on the crystals of larger dimensions as compared to the smaller ones, as can be seen in fig. 10.4. It seems from the growth experiments that lower temperature favours the development of ((001)) faces of the crystal. However, the reason for the formation of twinned crystals at lower temperatures is not clearly understood.

10.5 Conclusions

1. The controlled growth of single crystals of BaSO\textsubscript{4} and SrSO\textsubscript{4} in silica gel is reported.

2. The growth has been materialised by employing modified growth apparatus which yield better results.

3. The crystals seem to incorporate gel during growth.

4. Gel pH values between 6 - 9 give better crystals.

5. The habit of gel grown BaSO\textsubscript{4} and SrSO\textsubscript{4} crystals
has been found to be the same as that of these crystals grown by flux technique.

6. Growth at a temperature of 20° C resulted in the formation of twinned crystals.

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<th>Year</th>
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