CHAPTER – V

MICROSTRUCTURES OF CaSO$_3$ SINGLE CRYSTALS GROWN IN SILICA GEL

CHAPTER 5

MICROSTRUCTURES OF CaSO$_3$ SINGLE CRYSTALS

5.1 Introduction

Studies on microstructures of single crystals are very important in understanding about the mechanism of growth of the crystals. Eventhough the microtopographical structures of different faces of a crystal represent the conditions at the termination of growth, correlations of such structures on different faces give information about the history of growth of the crystals. Observation of the microstructures is indeed interesting to geological scientists, as the crystallization processes in the laboratory have some similarities with those occurring in nature. Thus the study of growth mechanism of crystals grown in gels might give a clue to the understanding of the growth mechanism of rock-forming materials.

A detailed study of microstructures of various crystals led Stransky [1]; and also Kossel [2] to put forward, independently, two-dimensional nucleation theory for the growth of crystals. Studies of surface structures on crystal faces have also proved helpful in establishing screw dislocation theory of crystal growth by Frank [3] and also in interpreting information concerning structure and behaviour of dislocations in crystals.

Previous two chapters (i.e., Chapters 3 and 4) describe the detailed studies made on the gel growth and characterization

of $CaSO_3$ single crystals. The present chapter deals with a detailed, yet precise, investigation carried out on the surface structures of silica gel grown crystals of $CaSO_3$ with the specific aim of understanding the mechanism of its growth.

5.2 Experimental Procedures

Calcium sulfite crystals were grown in silica gel at room temperature, at pH value of 4.5. The crystals were grown using various concentrations of feed solutions of Na_2SO_3 ranging from {0.1 to 1M}. Transparent crystals bounded by {001}, {101} and {210}, faces were obtained from the diffusion of the two reactants of $CaCl_2$ and Na_2SO_3 as described in Chapters 3 and 4. The crystals were thoroughly cleaned with ethyl alcohol and were coated with silver films in a vacuum coating unit. They were then examined under metallurgical and scanning Electron Microscope.

5.3 Observations and Discussion

5.3.1 ~~Special~~ Spiral Growth:

Crystals obtained using feed solutions of low concentration (below 0.2M) showed the presence of two different spiral structures on {001} faces as shown in figures 1 and 2. At lower concentration of the feed solutions, {001} faces are the slowest growing faces and hence they are larger in size than the other {210} and {101} faces. Observations of growth spirals on {001} faces of

calcium sulfite crystals at lower concentrations of feed solutions suggest that these faces might have grown by spiral growth mechanism. It is suggested that as gowth proceeds, internal stresses develop. Such internal stresses give rise to slip steps, thereby producing screw ledges on these faces and growth around such ledges results into spiral turns.

5.3.2 Growth Layers from the Edges of Large Steps on the Crystal:

It is general observation that the edges of the crystal or large steps on the crystal surface sometimes work as elegant centres for initiation of growth layers. Several examples illustrating this effect are observed on the { 001 } faces of crystals grown in silica gels using $CaCl_2$ and Na_2SO_3 as the reactants. Figures 3 and 4 show the starting of growth layers from the edges of $CaSO_3$ crystals. Figures 5 and 6 show the photographs of two typical crystals of $CaSO_3$ taken using scanning Electron Microscope (SEM). The growth layers on the { 001} face of $CaSO_3$ crystal are clearly seen at a higher magnification using SEM, in Figure 7. The growth layers from large steps on the crystal { 001} faces are shown in Figures 8 and 9. Sometimes growth layers start from all the sides of a crystal face and advance towards the centre of the face, which is clearly shown in Figure 10. The starting of growth layers from several points on the dark line marked AB in Figure 11, can be very clearly seen. The line marked AB is the edge of thick crystal

on which the growth layeres are seen. The figure shows a build up of material on the crystal edges with a fill in towards the centre indicating that edge nucleation was the predominant growth mechanism at higher concentrated feed solutions (Figs. 10 and 12).

The occurrence of step imperfections is a common feature observed on crystals grown with 1.5M feed solutions and often layers do originate from the imperfections on the steps. A beautiful example is provided in Figure 10 where step imperfections initiate growth layers.

5.3.3 Growth Layers from Liquid Inclusions:

Inclusions and tiny misoriented crystals do have their influence on the spreading of growth sheets on the host crystal face [4]. The most typical and widely observed growth pattern of such type is the one which looks like the back current formed behind a rock is a stream. Figure 13 shows an example of such a pattern. This pattern is derived from the two dimensional nature of spreading of growth layers. If growth continues, it may so happen that liquid drops or impurities get covered over by the growth layers in which case they get embedded in the body of the crystal and they affect the perfection. Sometimes growth layers started from the line shaped liquid inclusions as shown in Fig. 14.

5.3.4 Overgrowth on the Crystal Surfaces:

Sometimes overgrowths of quite large size (from a few angstroms to a few microns) were observed to be grown on the {001} faces of the host (primary) crystals. Figures 15 and 16 show overgrowths on the {001} faces in the form of square and spinel cord structures respectively. According to Buckley [5] overgrowth occurs owing to interruptions in the continuity of deposition due to changes in growth conditions, such as temperature changes or the temporary exhaustion of a solution after an active burst of crystalliz- ation.

5.3.5 Liquid Inclusions:

An instance of liquid inclusion on the {001} face of a crystal is shown in Figures 17 and 18. These inclusions are advancing along {010} direction. That the inclusions show a tendency to have {010} indicate that the surface energy of the {010} is less than that of any other plane. This indication agrees with the views of Seitz [6] and Wagner et al. [7]. Sometimes, at higher concentrations of feed solutions (> 1M), liquid inclusions with no crystallographic orientation have been observed as shown in Figure 19. Occasionally, triangular shaped liquid inclusions have also been observed as shown in Fig. 20.

Liquid inclusions are produced when an area of a crystal

face ceases to grow whilest the neighbouring areas continue to grow normally, then after a certain time the available liquid is enclosed, the reason of the cessation of growth may be adsorption of some impurity or some minor fluctuations in temperature during growth [8]. The probable liquids trapped into the crystals are, in the author's opinion, sodium chloride resulting as the by-product or reaction waste product during the crystallization of $CaSO_3$

5.4 Conclusions

1   It has been observed that a very low concentrated (below 0.2M) feed solutions, the crystals were grown by screw dislocation mechanism.

2   At higher concentrated (0.5 to 1.5M) feed solutions, layer growth mechanism is predominant. It has been observed that the growth layers initiate from the edges, steps and inclusions on the crystal surface.

3   Overgrowths of square and spinal cord type structures have been observed on the host crystal faces.

4   It has been observed that liquid entrapment is the main source of crystal defects in gel-grown $CaSO_3$ crystals.

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