Surface topographical studies of prism faces of barium copper oxalate single crystals

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Abstract. The present paper reports observations made on microstructures of gel-grown barium copper oxalate crystals. Growth spirals, growth layers, liquid inclusions and growth of microcrystallites are described and discussed in relation to the mechanism and conditions of crystal growth.

1. Introduction

The study of surface structures of crystal faces allows an understanding of growth and development of habit faces in particular and crystals in general. Sunagawa (1975) showed that surface microstructure of crystal faces is far more sensitive to differences in growth conditions than macromorphology. A detailed study of microtopography of various crystals led Stransky (1928) and also Kossel (1927) to put forward, independently, a two-dimensional nucleation theory for growth of crystals. Studies of surface structures on crystal faces have also proved helpful in establishing the screw dislocation theory (Frank 1949) of crystal growth and also in interpreting structure and behaviour of dislocations in crystals.

Recently we published detailed studies on gel growth and characterization of barium copper oxalate single crystals (Kasthuri and Mohan Rao 1992). The present paper deals with a detailed investigation carried out on surface structures of gel-grown crystals of barium copper oxalate to understand the mechanism of growth of these crystals.

2. Experimental procedure

Single crystals of barium copper oxalate were grown at ambient temperature and pH between 2.9 and 3.1, using sodium metasilicate of specific gravity 1.04. Typical crystals obtained are usually transparent, blue in colour, and cuboidal. Chemical composition of these crystals was determined by employing EDAX. The crystals have 51.3 and 48.7 atom. % barium and copper respectively.

X-ray diffraction studies of these crystals show that barium copper oxalate belongs to the triclinic system with $a = 6.5405 \text{ \AA}$, $b = 9.2019 \text{ \AA}$, $c = 10.9389 \text{ \AA}$, $\alpha = 85.45^\circ$, $\beta = 79.22^\circ$, $\gamma = 80.45^\circ$ and space group $P\bar{1}$. For microscopy, the crystals were thoroughly cleaned with the usual reagents and coated with silver film in a vacuum coating unit to enhance the contrast. The faces were then examined under a metallurgical microscope.

3. Observations and discussion

The crystal faces of barium copper oxalate exhibit a variety of growth features such as striations, growth hillocks and liquid inclusions.

Most of the faces are marked by horizontal striations parallel to the *b*-axis. Some of the striations are more pronounced while others are of normal character. Figure 1 is a photomicrograph illustrating horizontal striations on the prism face of a gel-grown barium copper oxalate crystal. It shows smooth as well as kinked striations which are closely spaced. The striations are observed to be widely spaced in some areas and bunched with unequal separations in others.

The striations are edges of growth layers comprising rectangular growth fronts observed on these faces. Such growth fronts are shown in figure 2. The longer sides of these growth hillocks are oriented along the edges of the corresponding prism face (see figure 2). It is suggested that such hillocks are formed as a result of a comparatively greater rate of advance of growth front of layers along the *b*-axis compared to that in a direction perpendicular to the *b*-axis. From figures 1 and 2 it may be suggested that independent growth takes place on the prism faces of barium copper oxalate crystals.

In addition to these rectangular growth layers, another interesting feature on these faces is the existence of hexagonal growth layers. One such case is shown in figure 3. Sometimes the growth hillocks act as growth centres, from which growth layers originate.

The reporting of growth hillocks on the faces of crystals dates back to 1899, when Daly (1899) reported hillocks on hornblende and interpreted them as etch hillocks. Hillocks observed by Williams (1932) were of the layer type and were interpreted as growth hillocks. According to Buckley (1951) all natural hillocks should be treated as ones produced during growth if they show a degree of symmetry corresponding

Figure 1. Horizontal striations on a prism face ($\times 200$).

Figure 2. Rectangular growth fronts on a prism face ($\times 100$).

Figure 3. Hexagonal growth layers ($\times 125$).

to that of the face. The rectangular and hexagonal growth hillocks we have observed on prism faces, with longer sides parallel to the b -axis, are in conformity with the outlines of the face on which they occur.

From these observations on prism faces of barium copper oxalate crystals (figure 3)

we are inclined to suggest that these prism faces initially develop and grow by spreading and piling of hexagonal growth layers. As a result of interaction of growth sheets on one prism face with those on neighbouring prism faces, they become rectangular.

It is interesting to note that in a few cases a variety of disc patterns similar to growth hillocks observed on the surface of cultured quartz crystals (Joshi and Vagh 1964; Hosaka and Taki 1981a, b) are seen on the prism faces of barium copper oxalate crystals. Figure 4 shows a magnified view of such island-like disc patterns observed on one of the faces. These patterns resemble impurities on the summit of a growth hillock and growth patterns similar to closed loops due to Frank–Read sources. The top surfaces of some of the discs look almost flat whereas some others are not. These patterns must have been formed towards the end of growth of the crystals.

Inclusions are produced when an area of a crystal face ceases to grow while neighbouring areas continue to grow normally, and, after a certain time, the available liquid is enclosed. The reason for cessation of growth may be adsorption of some impurity or some minor fluctuations in temperature during growth (Strickland and Constable 1973). In the present case, the liquid trapped in the crystals is probably HCl, the reaction waste product during crystallization of $\text{Ba}_x\text{Cu}_{1-x}\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$. An example of liquid inclusion on the as grown prism face of the crystal is shown in figure 5, in which the rings are due to interference effects.

Sometimes overgrowth of quite a large size was observed to grow on the prism faces of the crystals. Figure 6 shows a triangular overgrowth on a prism face.

According to Buckley overgrowth occurs due to interruption in the continuity of deposition, which in turn is due to change in growth conditions, such as temperature changes, or temporary exhaustion of the solution after an active burst of crystallization.

Figure 4. Island-like disc pattern on a prism face ($\times 250$).

Figure 5. Liquid inclusion on the as grown prism face of a crystal ($\times 125$).

Figure 6. Overgrowth on a prism face ($\times 250$).

4. Conclusions

- (i) At all concentrations of feed solutions, layer growth mechanism was predominant. It was observed that the growth layers initiate from the edges, steps and inclusions on the crystal surfaces.
- (ii) Liquid inclusion was the main source of crystal defects in gel-grown barium copper oxalate crystals.
- (iii) Advancing growth layers might produce guest crystals.

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