MICROTOPOGRAPHICAL STUDIES

5.1 Introduction

The history of the growth of crystals can be revealed by a careful observation of the as grown faces of the crystals. The faces of the crystal, being the last stage of its growth, reflect the characteristics of the growth process. A detailed study of the surfaces will give a lot of information. It is also possible to know the behaviour of the internal imperfections such as dislocations, stacking faults, etc., since they affect the surface patterns of a crystal to a great extent. The study of the surface features will throw light on the nature of temperature fluctuations, density gradients and other physico-chemical conditions during growth.

In the present study the surface features of the gel grown PSO, NPO and NSO crystals have been thoroughly investigated. Optical microscopy and AFM techniques have been utilized to study the nature of growth patterns and etching studies have been employed to reveal the dislocations. Mechanical strength of the crystals has been determined by microhardness measurements.

5.2 Morphology of the crystals

Mixed rare earth oxalate crystals of PSO, NSO and NPO grown in hydrosilica gel are hexagonal in shape. Their thickness is much smaller than the
width. The most developed face of these crystals is (100) which is perfectly smooth. These crystals have a cleavage plane perpendicular to the (100) face. Crystals with well developed faces are formed at the bottom of the gel column whereas the crystals at the top of the gel column are found to have irregular morphology. The average size of the crystals is about 2 mm x 1 mm x 0.5 mm. Spherulitic type of crystals are also observed. The origin of a spherulite is an aggregate of nucleation centres. The situation is generally observed in the case of crystals grown when acid concentration in the feed solution is negligible.

5.3 Microscopic studies

Preliminary observations of the surfaces of the grown crystals have been done using a powerful optical microscope, Lietz Metallux-3. The crystals were thoroughly washed before observation in order to make the surface clean. In this investigation more than hundred crystals were observed under the microscope and a few were selected for detailed study. The crystals of PSO, NSO and NPO show similar type of growth patterns and hence, the discussion is concentrated only on some typical crystals of PSO. In all the samples it is observed that the (100) face is predominant hence showing that the growth rate perpendicular to the direction of this face is minimum. Microscopic observations revealed that the faces of the crystal are generally smooth, but contain different types of growth patterns.

Figure 5.1 shows a typical case of (100) face of PSO crystal. The morphology of the crystal is hexagonal. It can be seen that the face is relatively plane, but have very thin growth layers parallel to the two end faces. It is interesting to note that there is a very thin narrow line running parallel to the major axis. This may be a crack produced during the growth or after the cessation of the
growth. These type of lines are commonly observed on (100) face of the crystals. Growth layers of similar nature but with large step height are observed in some crystals. A representative of which is shown in Figure 5.2.

The growth layers observed on the surface is produced by secondary nucleations and spreading of layers from its growth centres. The thick growth layers may be due to the higher concentration of the nutrient and the thin layers due to lower concentration. Crystals having growth layers with different step heights indicate that even in the same growth environment, micro regions can exist with different concentrations.

When growth layers originating from two regions interfere with each other, very thick growth patterns are observed which are illustrated in Figure 5.3. As the growth process advances, multiple nucleation centres may originate either from defect sites or by the interaction of foreign particles [1,2]. This will result in the formation of growth hillocks (Figure 5.4). Point and flat topped hillocks are observed. The flat hillocks may be formed due to the dislodging of foreign particles in the middle of growth process. On further growth the hillocks will interfere with each other, and result in mottled nature of the face. Individual crystallite aggregates can be formed on the surface as shown in Figure 5.5.

A typical example of guest crystals growing on the surface of an already grown host crystal is shown in Figure 5.6. Microcrystals attached on the surface might have grown along with the main face on which it is attached and produces its impression on the surface when detached at a later stage.
Fig. 5.1 (100) face of PSO crystal with thin growth layers

Fig. 5.2 (100) face of PSO crystal with thick growth layers (x 50)

Fig. 5.3 Interaction of a thick growth layer on (100) face (x 200)

Fig. 5.4 Mottled nature of (100) face

Fig. 5.5 Crystallite aggregates in (100) face (x 200)

Fig. 5.6 Impression of a detached foreign crystal (x 100)
5.4 Microtopography by AFM

Microscopic investigations revealed the general nature of the crystal surface. But microfeatures may escape from the observation even at higher optical magnifications. Recently, a new technique, Atomic Force Microscopy (AFM), has been developed which can be profitably utilized to reveal the minute surface details in nanoscale [3]. Details of this technique has already been given in Sec. 3.3. The bulk observations which has been noted in optical microscopy can be studied in nanoscale using this powerful technique.

Some typical crystals were selected and studied critically using the AFM technique. These crystal surfaces show very interesting features under high magnification. Apparently plane regions on the surface show minute distinct features. Figure 5.7 shows a typical AFM photograph. Carefull examination of the photograph reveal that this apparently smooth surface have undulations which can be detected from the intensity variations on the crystal surface. These undulations may be due to thin layers having thickness of a few molecular dimensions. It can be seen that a shallow groove is running parallel through the centre of the (100) face. This shallow groove is a typical feature of most of the crystals which has been already mentioned in the earlier section. This groove may be due to the micro-cracks formed after the cessation of growth. The growth layers spreading on the surface does not interfere with the groove which strengthen our inference that the microcracks are originated after the cessation of the growth.

Figure 5.8 gives another example of microcrack which has more depth. The lip of the crack in this particular case show a step. This may be due to the removal of material due to natural etching while it was in the growth stage. Another example is shown in Figure 5.9 in which very deep shallow grooves which
Fig. 5.7 AFM photograph showing nanolayers and crack of NPO crystal

Fig. 5.8 AFM photograph of a large crack on the surface of NPO crystal
Fig. 5.9 AFM photograph of parallel cracks on the surface of NPO crystal

Fig. 5.10 AFM photograph of spreading layers on the surface of NPO crystal
Fig. 5.11 AFM photograph showing hillocks on the surface of PSO crystal

Fig. 5.12 AFM photograph showing cluster of hillocks on the surface of PSO crystal
run parallel to each other can be seen. It is further proved from the etching studies that these grooves are due to microcracks, and is discussed in the next section.

AFM studies also revealed thin growth layers on the surface. Figure 5.10 shows a number of thin growth layers originating from the edge of a shallow depression. The growth layers originating from a nucleation centre spread while new layers started to nucleate from the same centre. This process resulted in the formation of patterns as revealed in Figure 5.10. These growth layers are uniform in thickness and of a few nanometers.

Figure 5.11 shows a relatively plane surface but having a few hillocks. The height of the hillocks vary from 20 nm - 100 nm. These hillocks may be due to isolated two dimensional nucleation centres. Sometimes it can be seen that growth hillocks are crowded in a region. A typical example is shown in Figure 5.12. The height of the hillocks vary considerably. The present observation show that multiple nucleation centres originate even at molecular level. These nano level growth centres develop into micro level features with flat and pointed hillocks.

5.5 Etching studies

Although the theoretical treatment of nucleation and crystal growth makes the simple assumption that the crystal lattice beneath the growth surface is perfect, this is not the real case. The concept of an ideal crystalline solid is valid only at absolute zero temperature. At any finite temperature, a certain configurational disorder is introduced into the developing crystal and are termed as defects. The major defect encountered in the formation of a crystal is dislocations. A detailed study of the behaviour and distribution of the dislocations in a crystal is important since:
The presence of dislocations profoundly influence the physical and chemical properties of a crystal such as mechanical strength, electronic and ionic conductivity, optical properties, etc.

It play an important role in crystal growth.

Hence, either to understand how the growth process influence the perfection of the crystals or to produce crystals having the required perfection for practical applications one must determine the nature and number of dislocations in a grown crystal.

A number of techniques have been developed to study the distribution and density of dislocations and to determine their properties. Amelinckx [4] has reviewed the methods for the direct observation of dislocations. Of these various methods, etching is the simplest method for the detection and characterization of these defects. The first direct proof of the applicability of etching to reveal dislocations was given by Gevers et al. [5] and Horn [6]. The potentiality of etching in the study of the dislocations is evidenced by the voluminous literature in this field [7-10].

The method of etching consists in immersing the crystal in a suitable medium which may be a pure liquid, a solution or gas. If the selected medium is a suitable etchant for the crystal, dissolution takes place. The dissolution is not uniform but it begins only at certain points on the surface and proceed more rapidly in some directions than in others. If the etching action is stopped at the right time, the uniform solid surface is found usually covered with tiny, geometrical figures, often referred as etch pits. The shape of etch figures varies with the nature and concentration of the solvents, time and temperature, but is strictly related to the molecular configuration of the crystal surfaces.
5.5.1 Formation of dislocation etch pits

The kinetic aspects of etching process and the geometry of etch pits have been the subject of extensive experimental and theoretical studies [11]. Dislocation etch pits are formed when the etching reaction is sensitive to the energetics of the atoms at the surface and to their geometric configuration. The initiation of etch pit has been considered as a nucleation process analogous to that in crystal growth. This nucleation may occur at the emerging point of the dislocations. Nucleation of etch pits at dislocations has been attributed to the elastic strain associated with the dislocations which causes a decrease in the activation energy for nucleation [12]. Dissolution, being the reverse process of growth, is believed to occur by the removal of molecular steps. When the crystal is subjected to any physical or chemical process, the weakly bound growth units at the dislocation sites may dissociate from the crystal thereby forming an etch pit. Hence etch pits essentially reveal the emerging point of dislocation in the crystal surface. The number of etch pits give a direct measure of dislocation density. Since they are having a certain depth, they also provide information about the nature, configuration and inclination of dislocations [13].

Etch pits do not necessarily correspond to dislocation intersections with the surface. The etch pits which are not associated with dislocations usually does not reappear after repeated etching, as they are formed by shallow defects. On the other hand etch pits associated with dislocations reappear upon repeated etching, since the dislocation line cannot terminate within the crystal [14]. Successive etching will result in widening and deepening of the etch pits and this reveals the sites of dislocations.
5.5.2 Dislocation studies of the crystals

Dislocation investigations have been carried out on the crystals of PSO, NSO and NPO. Since the molecular configuration of all the crystals are the same, it is found that the etching characteristics, nature of etch pits, etc. of all the crystals are identical. Hence a detailed description of any one of these samples could represent the general nature of dislocations of the mixed rare earth oxalate crystals. In the present case PSO crystals are selected for this purpose.

5.5.3 Cleavage surfaces

Figure 5.13 shows the general characteristics of cleaved matched faces of PSO crystal. From the figure it is clear that there is a perfect correspondence of cleavage lines on two matched surfaces. The general topography of these cleaved matched faces show the following nature.

1) Major portion of the surface is remarkably flat.
2) The cleavage steps are of various heights.
3) Thinner cleavage lines join together to form thicker cleavage lines i.e., they form the so called river patterns.

In most of the crystals a funnel like pattern is observed which may be a bulk defect developed by the introduction of micro defects during early stage in its growth.

5.5.4 Selection of the etchant

There is no hard and fast rule in selecting the etchant suited for a particular crystal. Hence one has to resort to trial and error methods to ascertain the capability
of the etching reagent in delineating the dislocation sites. The formation of the etch pits depend upon many physico-chemical factors governed by the characteristics of the etchant and the crystal surface.

A number of suitable chemicals were tried as part of the investigations to find the most suited etchant for these mixed rare earth oxalate crystals. The concentration of the reagents, time of etching, and temperature were varied for the etching studies. After a series of experiments, HNO₃ was found to be the most suitable for revealing the etch pits of these crystals. Various concentrations of HNO₃ were tried in order to produce etch pits having regular morphology. It was found that HNO₃ having concentrations in the range 0.6 M - 1 M gave the best results.

5.5.5 Etch pits on (100) face

Carefully selected crystals with good faces were immersed in 1 M HNO₃ for some time and rinsed with distilled water, dried, and examined under a microscope. It was observed that within 15 seconds visible pits originated on the surface. The etch pits so obtained on the natural face (100) of PSO crystal is shown in Figure 5.14. A detailed observation on the pits can be concluded as:

1) Pits are perfectly oriented in (110) direction.
2) Some are symmetrical with respect to their outline whereas some are asymmetrical.
3) Both point bottomed and flat bottomed pits are observed.
4) Some pits are terraced.
5) Occasionally parallel grooves are seen running over the surface.
Fig. 5.13 Cleaved matched face of PSO crystal (x 50)

Fig. 5.14 General nature of etch pits on (100) face (x 200)

Fig. 5.15 (100) face etched for 20 seconds (x 50)

Fig. 5.16 Continuous etching of (100) face for 40 seconds (x 50)

Fig. 5.17 Continuous etching of (100) face for 60 seconds (x 50)
In order to study the correlation between the etch pits and dislocations, a crystal was etched for 20 seconds and the resulting pattern is shown in Figure 5.15. This face was repeatedly etched twice in steps of 20 seconds. Figures 5.16 and 5.17 show patterns resulting from successive etching. The following points are noteworthy.

1) Development of the pits are uniform
2) No new pits are found to form during successive etching.
3) The pits continue to develop in depth and in lateral dimensions.
4) Some of the flat bottomed pits disappeared in the final stage.

5.5.6 Etching of (110) face

The (110) face of a crystal was etched for 20 seconds initially and the resulted pattern is shown in Figure 5.18. The same face was successively etched in steps of 20 sec. Figures 5.19 and 5.20 show the corresponding patterns. It can be seen that the pits are trapezoidal in geometry. Their outlines are straight and have more depth and hence appear to be dark. Figure 5.21 however showed that these pits are point bottomed, which include symmetrical as well as eccentric pits. Flat bottomed pits are rare in these faces. Point bottomed pits are found to be developing in lateral as well as vertical dimensions during successive etching.

5.5.7 Etching of cleaved surface

Perfectly cleaved crystal provide fresh surface for dislocation studies and hence can be conveniently used to investigate the distribution and content of dislocations threading through the crystal lattice. Matched cleaved surfaces etched for 20 sec. are shown in Figures 5.22 and 5.23. Point bottomed pits can be seen
Fig. 5.18 (110) face etched for 20 seconds (x 200)

Fig. 5.19 Continuous etching of (110) face for 40 seconds (x 200)

Fig. 5.20 Continuous etching of (110) face for 60 seconds (x 200)

Fig. 5.21 Eccentric etch pits on (110) face (x 200)

Fig. 5.22 Etch pits on a cleaved surface (x 100)

Fig. 5.23 Etch pits on the cleaved matched surface (x 100)
which have a perfect one to one correspondence on the matched surface. It is also found that the point bottomed pits continue to grow on further etching conforming that the pits are due to dislocations.

5.5.8 Discussion on etching studies

Etching method is a powerful tool to reveal the dislocations in a crystal. The regions around the terminating points of dislocations have more energy than its surroundings. While etching, the probability of having dissolution at these sites will be more than that of its surroundings [15]. This will result in the formation of visible etch pits at the point of attack. Further etching will result in continuous development of the etch pits if it is a linear defect. This is the thing happening on continuous etching.

Etching of the natural faces and cleavage faces show that the etch pits develop laterally and in perpendicular directions. When a crystal is cleaved the linear defects which pass through the body will cut into two halves which can be revealed by etching the cleaved surface. In this case perfect correspondence will result. The observations on the etching of the matched, cleaved surface of PSO crystal support this. The etch pits on the cleaved surface is found to develop further on continuous etching which show that the dislocations are indeed, revealed by these pits. The symmetry of the etch pits show that the dislocation is perpendicular to the surface [16] and eccentricity observed in the case of some pits reveal the inclined nature of dislocations [17]. The terraced pits are due to the impurity segregation during the etching [18]. Etch pits can also be produced at the sites of impurities and point defects. When such sites are etched flat bottomed pits are expected. These flat bottomed pits will disappear on further etching as noted in the observations.
HNO₃ is found to be an ideal etchant to reveal dislocations in the PSO, NSO and NPO crystals. This etchant is equally effective in revealing dislocations in all faces. The flat bottomed pits are abundant in the basal plane but very few in the (110) plane. This may be due to the probability of higher chance for the segregation of impurities on this plane due to the nature of the atomic arrangements.

5.6 Microhardness studies

Hardness testing studies provide useful information concerning the mechanical behaviour of materials. It is the fastest and simplest type of mechanical testing. Various other mechanical characteristics of the material such as toughness, brittleness, etc. can be investigated by hardness measurements [19]. Most hardness tests produce plastic deformation in materials and all variables which affect plastic deformation affect hardness [20]. The hardness is a measure of the ability of a material to resist permanent deformation. The hardness determination is normally made using a mechanical test which gives a measure of the ease with which the material can be locally deformed. Usually an indentation or scratch test is performed under defined conditions. The microscopic hardness indentation are made with very small loads. The size of the indentation or scratch is related to the applied load and strength of the material. The Vickers microhardness test is one of the most common and reliable methods for hardness measurements. There are many reports of Vickers microhardness measurements on various crystals [21,22].

The dependence of Vickers microhardness $H_v$, on applied load show different behaviour for different materials. The variation of microhardness with increasing load may be classified into four groups [23-26].
i. $H_v$ remains unaffected
ii. $H_v$ decreases
iii. $H_v$ increases
iv. $H_v$ shows complex variation

Various laws have been suggested to explain the variation of microhardness with load [27].

5.6.1 Microhardness studies of mixed rare earth oxalate crystals

Perfectly plane crystals of PSO, NSO and NPO were selected for the microhardness measurements. Indentations were carried out, using a Vickers pyramidal indentor for various loads ranging from 5 to 100 gms. The duration of the indentation time was kept constant at 10 seconds. In all experiments the distance between the two indentations was kept three times greater than the diagonal length of the indentation mark in order to avoid any mutual influence of the indentations. For each load, several indentations were made and the average value of the diagonal length of the indentation mark was used to calculate the microhardness. The hardness number $H_v$ of the crystal was calculated using the relation:

$$H_v = \frac{1.8544 \times p}{d^2} \text{ Kg/mm}^2.$$

Figure 5.24 represent the variation of microhardness with load for PSO, NSO and NPO crystals. It can be seen from the figure that $H_v$ increases as load increases for all these crystals.

The increase in hardness with load is primarily caused by the work hardening of the surface layers [28]. Above 50 gms, cracks start propagating from the indentation mark.
Fig. 5.24 Variation of microhardness with applied load
References

6. Horn, F.H., Phil. Mag., 43 (1952) 1210


