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Microtopographical investigations on flux grown $ErFeO_3$ crystal surfaces

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Surface structures on {100} surfaces of flux grown $ErFeO_3$ crystals have been studied, using high precision optical techniques. They include elliptically shaped growth hillocks, tiny mole hills, growth pyramids, attached microcrystals, triangular, rectangular and polygonal cavities, cracks, tilted portions and misfit boundaries. The observations indicate that micronuclei may form in the crucibles or at the surfaces of growing $ErFeO_3$ crystals by crystallization from flux. Misfit boundaries, tilted portions, microcrystals and cracks are found to act as preferential sites for the nucleation of centres of growth.

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1. Introduction

Both macromorphology (crystal habit) and micromorphology (surface microtopography of crystal faces) of crystals grown from the vapour or from solution are determined by two factors, structural and environmental. Thus, one can obtain information pertaining to both, in addition to information relating to growth and dissolution mechanisms of crystals, through surface topographical investigations. These can lead us also to a fundamental understanding of the relation between crystalline quality (perfection) and various parameters of growth. The study is important particularly because in the case of most crystal growth techniques one does not know exactly what happens while the crystal is growing on account of practical difficulties in watching the crystal *in situ*, and thus there is no alternative but to use indirect means, such as these studies, to obtain information concerning growth mechanisms and dissolution processes. In this respect flux-grown materials are no exception: for example, the growth of $ErFeO_3$ crystals involves very high temperatures and the growing system remains sealed. To the best of our knowledge, there has been no work reported so far on the microtopography of $ErFeO_3$ crystals. In this paper observations on {100} faces of flux-grown $ErFeO_3$ crystals are described.

2. Experimental details

The $ErFeO_3$ crystals used in the present study were prepared using the fluxed melt technique. 22.9 g of Er_2O_3, 9.8 g of Fe_2O_3, 2.4 g of B_2O_3, 45.6 g of PbO, 64.8 g of PbF_2 and 1.0 g of PbO_2 were mixed by stirring on a sheet of paper, then pressed into a 50 cm^3 platinum crucible with a closely-fitting lid. Alumina powder was packed around the crucible in a refractory brick support. The crucible was heated to 1290° C in a muffle furnace with heating elements on both sides which provide a small negative temperature gradient of 2 to 3° C over the crucible. The temperature was held at 1290° C for 16 h and then reduced to 850° C at the rate of 2° C per hour. The material was separated from the crucible by tapping gently with a small hammer. The crystals were cleaned by heating in 20% nitric acid. $ErFeO_3$ crystals up to 1 cm on edge were obtained using a 50 cm^3 crucible. The composition given above yielded 24.3 g of $ErFeO_3$ crystals from a 50 cm^3 crucible.

The surfaces of the crystals were thoroughly cleaned and then coated with the optimum thickness of thin films of silver in a high vacuum coating plant, to enhance the contrast. The crystal surfaces were then studied under a universal metallurgical microscope Neophot-2 of Carl Zeiss Germany. Up-to-date means of optical investigation like multiple-beam interference [1], light pro-

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file [2] and phase contrast microscopy [3] were also employed wherever necessary.

3. Observations

3.1. Thin and thick growth fronts

Usually $\{100\}$ faces of $ErFeO_3$ crystals show the presence of both thin and thick growth layers originating from a number of growth centres. The growth layers are very thin and closely spaced near the initiation centres from which they are generated but get thicker and more widely spaced as they move further away from them. At times, the growth layers are so thin that their presence is detected only when the surfaces are observed under a phase contrast microscope. Usually the nucleus centres radiating out growth layers on the face are many and well distributed over the whole surface. Sometimes thick growth bands are observed near the edges and corners of $\{100\}$ faces.

3.2. Hillocks

Hillocks already present on as-grown crystal faces or produced by etching crystals in the laboratory have been reported in the case of several crystals [4–20].

During the present investigation it was observed that practically every $\{100\}$ face that was examined had some kind of hillocks, although their density differed in different cases, being of the order of $10^5\,cm^{-2}$ in crowded regions. In the most crowded regions the density was so high that it was very difficult to estimate it accurately especially in the case of very tiny mole hills. Fig. 1 shows part of a $\{100\}$ face exhibiting elliptical shaped hillocks and very tiny mole hills spread all over the face. Interferometric examination revealed that the heights of the hillocks vary between 0.5 and 6 light waves. The longer axis of the hillocks is observed to be parallel to the c-axis of the crystal.

In some cases hillocks are closely spaced and arranged in the form of an array. Fig. 2 offers an example of a closely spaced row of hillocks; the row being in a direction parallel to the edges of intersection between the $\{100\}$ face and $\{001\}$ plane, i.e. perpendicular to the c-axis.

From these observations, it can be inferred that elliptical hillocks are characteristic features of $\{100\}$ faces of flux-grown $ErFeO_3$ crystals.

In general, the growth layers composing these hillocks, especially near the centres of initiation, were very thin and closely spaced, making resolution difficult. However, a few hillocks, on close examination, displayed spiral ramps. The faces studied in the present investigation were remarkably brilliant and lustrous and the hillocks reported here are strictly oriented. These observations suggest that they may be growth hillocks, having possibly formed at the sites of screw dislocations.

3.3. Microcrystals and cavities

Since the crystal surfaces are the places where all phenomena concerning crystal growth and dissolution are most vividly reflected, microtopographical study of crystal surfaces leads to an understanding of the agencies which contribute to their growth and development [21–34].

During the course of the present investigation,

Figure 1 Elliptical hillocks and very tiny mole hills, × 45.

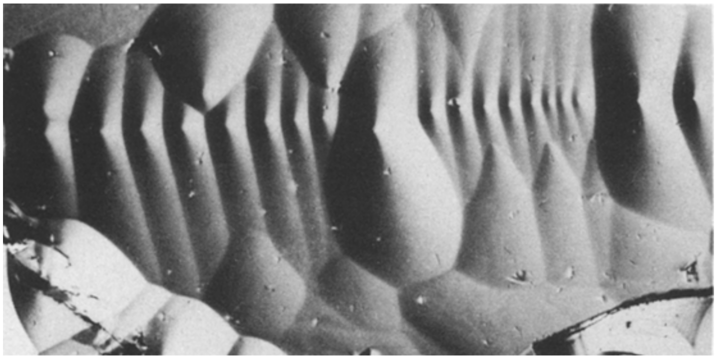

Figure 2 A row of closely-spaced hillocks, X 90.

it is observed that microcrystals attached to the growing host faces of $ErFeO_3$ crystals play the role of growth nuclei. Fig. 3 is a photomicrograph showing growth pyramids on $\{100\}$ face of an $ErFeO_3$ crystal. The growth layers composing the almost elliptical shaped pyramids are clearly visible in the photomicrograph. Because of the large size and great height, the summit and the base of these pyramids could not be simultaneously brought into focus with precision. However, close inspection of the summit of these pyramids could not be simultaneously brought into focus with precision. However, close inspection of the summit of these pyramids revealed the presence of microcrystals acting as centres of growth and generating elliptically shaped growth layers, thus creating extraordinary regions such as pyramidal growth where growth rates are faster than in other regions. Fig. 4 is a photomicrograph of one of the pyramids of Fig. 3 taken at a higher magnification, showing initiation of growth layers at one of the ends of a misoriented attached microcrystal with a rectangular boundary. Every growth pyramid of Fig. 3, when examined under the microscope, was found to have a microcrystal at the point of its initiation.

Microcrystals acting as nucleation centres were observed on the faces of a number of $ErFeO_3$ crystals. Most of the microcrystals were found to be rectangular in outline; however, some, though very few, were found to have a triangular outline. The micronuclei may stimulate growth of the concerned host faces of $ErFeO_3$ crystals as is clearly evidenced by the observations of the type of Fig. 4.

It is possible that a microcrystal may get attached to or nucleate at the growing host face at some stage of growth but may later get detached from it. In this situation, the detached microcrystal is expected to leave a cavity on the host face. Such cavities of different shapes and structures were observed on some of the $\{100\}$ faces of $ErFeO_3$ crystals.

The presence of misoriented crystals will induce internal strains which consequently may lead to

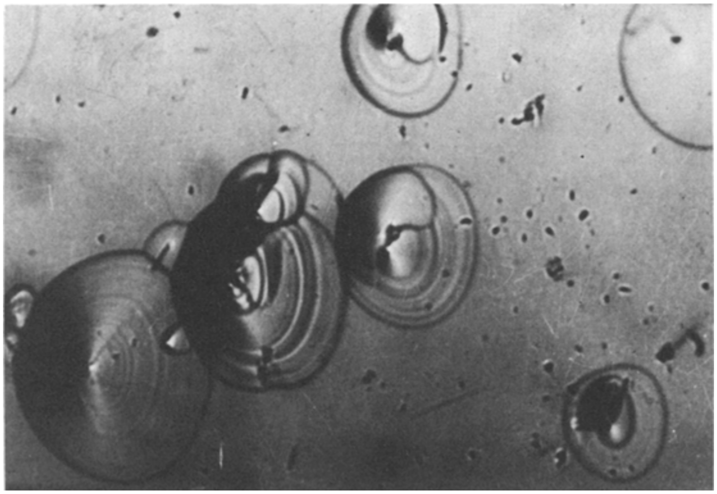

Figure 3 Growth pyramids composed of elliptical growth layers X 75.

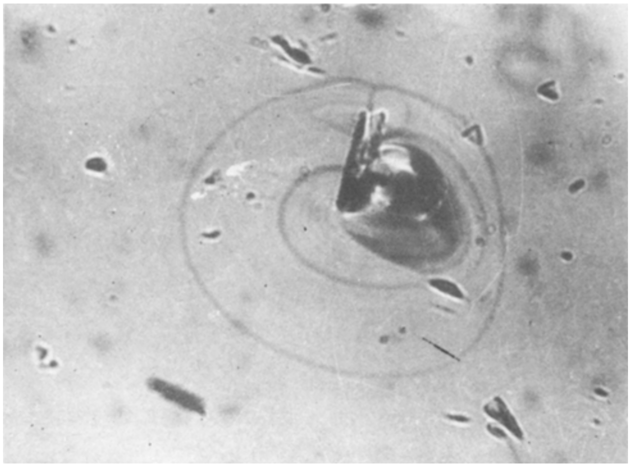

Figure 4 Initiation of growth layers on the host face by one of the ends of a misoriented attached guest microcrystal having nearly rectangular outline, × 150.

development of cracks in the crystals. Fig. 5 is a photomicrograph showing a region near the cavity which was produced as a result of detachment of a microcrystal. It shows a crack (AB) having developed in the crystal face either during attachment of the microcrystal or due to its detachment from the host crystal face. Part of the cavity is seen on the right hand side of Fig. 5.

3.4. Cracks and misfit boundaries

Many $ErFeO_3$ crystals exhibited cracks on their surfaces. Some cracks were found to be very deep whereas some were found to be almost scratch-like. It was found that whether it be a fissure-like crack or a scratch, these may lead to creation of growth centres. Fig. 6 shows a fissure-like crack (AB). Growth layers have originated (on the top right of the figure) from a nucleus centre lying on the edge of the crack, which appears to have developed before growth ceased. Fig. 7 shows a part of an irregular scratch-like crack on an $ErFeO_3$ crystal face. In fact, the crack had no definite orientation but had propagated in zigzag fashion right across the whole face. It is interesting to see the centres of initiation of growth hillocks all along the crack, indicating that the crack has created centres of preferential growth all along it.

Some faces of $ErFeO_3$ crystals exhibited the presence of lines of discontinuity. On close examination, it was found that some lines of discontinuity were in the form of linear strips slightly tilted with respect to the main face. Fig. 8 is a photomicrograph showing one such strip slightly misoriented with respect to the main $\{100\}$ face.

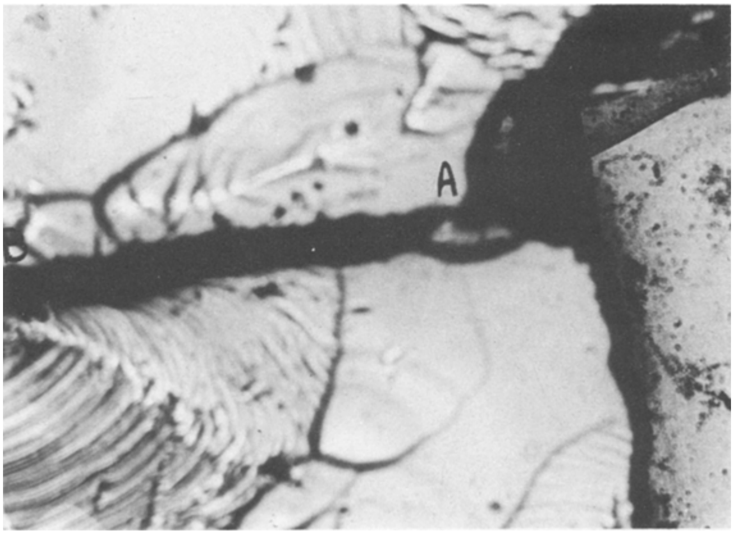

Figure 5 A photomicrograph showing a region near the cavity displaying the development of a crack on the crystal face as a result of attachment or detachment of the guest microcrystal from the host crystal face, × 50.

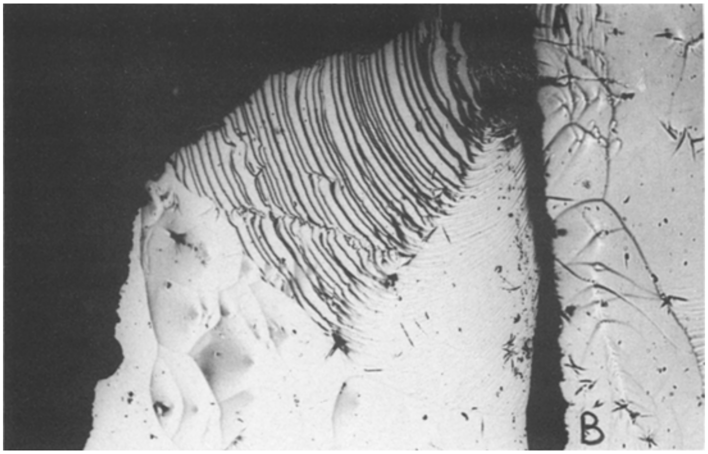

Figure 6 A fissure-like crack AB on the surface of an $ErFeO_3$ crystal. A growth pyramid having its centre of initiation on the edge of the crack is seen, × 45.

The misoriented strip was found to be in a direction making an angle of 45° with the edges of intersection between the (100) and (001) faces. On close examination with an oil immersion objective, it was found that there are growth centres on each side of the rectangular strip. A light profile, taken across the strip and the hillocks along it, confirmed that the structures along the strip are hillocks and that the strip is slightly tilted with respect to the main face.

Fig. 9 shows {100} face of another $ErFeO_3$ crystal. One finds a misfit boundary AB separating the two portions of the surface. There are growth pyramids on the surface lying on the right hand side of the misfit boundary, whereas the surface on the left side is devoid of any growth structures. It is interesting to find that the growth layers generated by nucleation centres on the right hand surface have not crossed the boundary and have remained confined to their parent surface. The growth centres of these pyramids (except that of the largest) lie very close to the misfit boundary. Here, this is a boundary between two crystals which have joined together.

4. Conclusions

1. The surface structures of the {100} faces of $ErFeO_3$ crystals include almost elliptically shaped growth hillocks, tiny mole hills, growth pyramids, attached microcrystals, triangular, rectangular and polygonal cavities, cracks, tilted portions and misfit boundaries between coalesced crystals.

2. It is possible that micronuclei forming in the crucibles or at the surfaces of growing $ErFeO_3$ crystals initiate the formation of microcrystals. The attached guest microcrystals initiate and stimulate growth of the host faces of $ErFeO_3$ crystals. The attachment of microcrystals followed by their detachment from the host surfaces of $ErFeO_3$ result in the formation of polygonal cavities of different shapes and structures.

3. $ErFeO_3$ crystal surfaces show the presence of

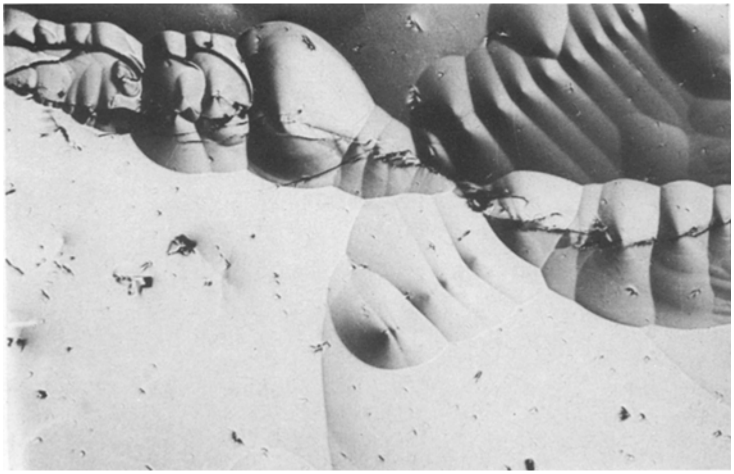

Figure 7 Photomicrograph showing part of an irregular scratch-like crack. Centres of initiation of growth hillocks lying all along the crack are clearly visible. × 90.

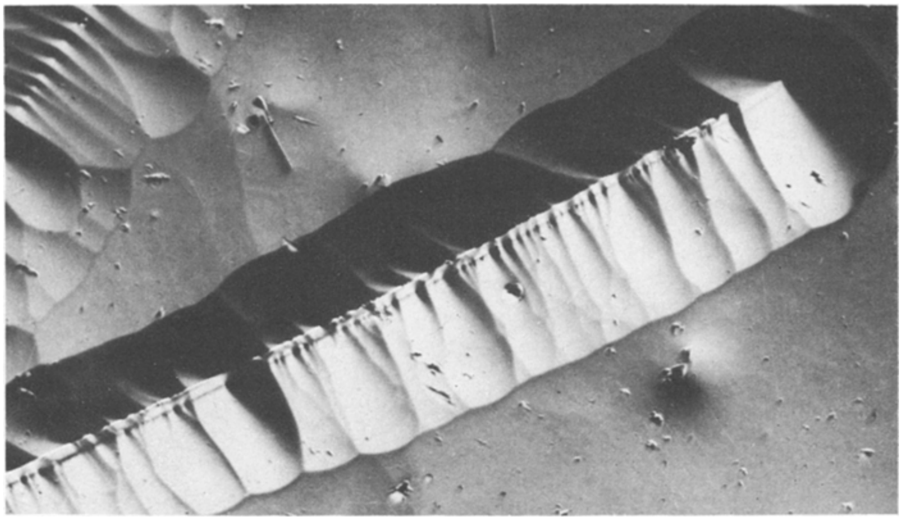

Figure 8 A photomicrograph showing a linear strip slightly misoriented with respect to the main $\{100\}$ face of an $ErFeO_3$ crystal, × 125.

misfit boundaries, tilted portions and cracks. Nucleation centres develop preferentially along the boundaries of tilted portions and cracks.

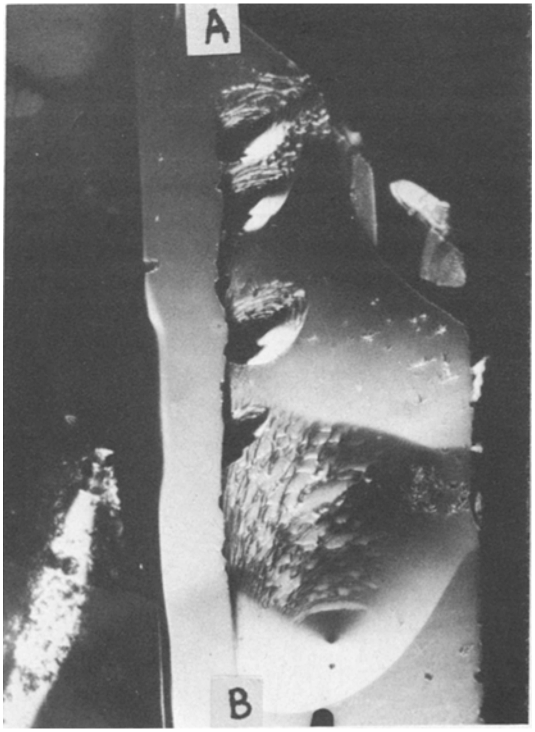

Figure 9 A misfit boundary AB separating the two joined parts of $\{100\}$ faces of $ErFeO_3$ crystals. Growth pyramids on the right hand side of the misfit boundary, and the surface on the left-hand side of it devoid of any growth structures, are clearly seen, × 50.

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