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An electron channeling study of polycrystalline YBa2Cu3Ox

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Abstract

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Keywords

Crystal structures, Crystallographic defects, Polycrystalline material

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An electron channeling study has been done on large grained $YBa_2Cu_3O_x$ samples. Selected area channeling patterns (SACP) were used to examine several dozen grains on electropolished surfaces and it was demonstrated that (a) the twin planes observed in polarized optical light microscopy lie parallel to {110} crystal planes, and (b) the long flat sides of high aspect ratio grains are formed by basal planes, and the shorter sides are formed by either (010), (100), or {110} planes. A majority of the large grains examined were found to contain subgrains, misaligned by 0.5°–1° and ranging in size from less than 3 to 20 μm. The origin of the subgrains is not understood.

I. INTRODUCTION

The high-temperature superconducting oxide, $YBa_2Cu_3O_x$, displays some interesting crystallographic features which may play a critical role in controlling some of its superconducting properties. For example, optical and transmission electron microscopy (TEM) show that the individual grains are composed of finely spaced parallel twin packets and there is some experimental and theoretical evidence that the T_c value may be enhanced in the vicinity of the twin boundaries.[1] TEM studies show that the twin boundaries lie along {110} planes with a spacing generally in the range of 20–80 nm.[2-6] Optical microscopy with polarized light reveals twin planes having a considerably larger spacing[7] and the relationship between the optical and TEM twin boundaries has not been clearly established. Studies on small single crystals[8,9] have shown that the optical twin boundaries in such crystals also lie along {110} planes. With selected area electron channeling patterns (SACP) obtained using the scanning electron microscope (SEM), it is possible to obtain information on the crystallographic orientation of the individual grains on polished bulk samples for grain sizes as small as 1–2 μm. Hence, it should be possible to use SACP techniques to verify the common assumption that the optical twin boundaries of polycrystalline $YBa_2Cu_3O_x$ also lie along {110} planes.

The grain boundaries of polycrystalline $YBa_2Cu_3O_x$ tend to be flat, and thus the individual grains appear predominantly as flat sided polygons on a polished surface. Many grains appear as elongated rectangles, and these will be referred to as high aspect ratio grains. The dominant facet plane of the small flux-grown single crystals[8,10] are the (001) basal planes, and it has generally been assumed that these are the long flat boundaries on high aspect ratio grains found in polycrystalline arrays. Recent TEM work by Nakahara *et al.*[11,12] has confirmed that many flat boundaries are basal planes and they suggest that these boundaries may be detrimental to the J_c properties because the larger thermal contraction in the *c* direction will produce normal tensile stresses at such boundaries. With the SACP technique it is possible to examine a large number of grains on a polished bulk sample and obtain information on the crystallographic habit of the long flat boundaries. This paper presents an SACP study of large grained $YBa_2Cu_3O_x$ samples which examines both the questions of the habit plane of the optical twin boundaries and of the long flat boundaries of high aspect ratio grains.

II. EXPERIMENTAL METHODS

Samples of $YBa_2Cu_3O_x$ were prepared by mixing and grinding dried powders of $BaCO_3$, Y_2O_3, and CuO, pelletizing and heating in air for 24 h at 890 °C. The pellets were ground and repelletized and again heated at 890 °C for 24 h in air. Finally, the pellets were ground again, repelletized, and heated in flowing O_2 for 3 days at 1000 °C. The samples were cooled at 3.5 °C/min, held at 500 °C for 1 h, and then furnace cooled to room temperature. After this treatment the pellets had a density of 5.9 g/cm^3 (94% theoretical), and were x-ray pure $YBa_2Cu_3O_x$. Field cooled measurements in a squid dc magnetometer gave a T_c onset at 92 K with a sharp rise to a maximum Meissner flux exclusion of 45% at 85 K. The processing produced a large grained material as illustrated by Figs. 2(b), 5, and 6(a).

Specimens were prepared for optical and SEM examination by a diamond polishing technique which has been described in detail elsewhere.[13] The electron channeling patterns obtained from as-polished samples were not sharp, apparently due to a damaged surface layer produced by the mechanical polishing. Therefore, the samples were electropolished in a solution of 1.5% perchloric acid, 3.0% water, and 95.5% methanol at − 80 °C. A polish time of 60–100 s produced surfaces which gave sharp channeling patterns. The selected area channeling patterns were obtained using the deflection focusing method on an SEM which had been modified to allow patterns covering about 8° to be obtained from an area as small as 1–2 μm.[14] The modification involved a dynamic correction to the final lens current to reduce spherical aberration and this was accomplished using spiral rather than rectilinear scanning. All of the patterns were taken at a beam voltage of 18 kV and a working distance of less than 1 mm using specimen current imaging. The conditions produced patterns having an angular spread of 3.9 °/cm.

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III. RESULTS AND DISCUSSION

The crystal structure of $YBa_2Cu_3O_x$ is orthorhombic with $a = 3.823$ Å, $b = 3.886$ Å, and $c = 11.681$ Å. The resolution of the channeling patterns is inadequate to resolve effects due to the very small difference in the magnitude of a and b, and therefore the patterns appear tetragonal.

A. The channeling map

The standard triangle for a tetragonal system involved a map having poles of ⟨001⟩, ⟨110⟩, and ⟨100⟩ at its three corners. Figure 1 presents the $[\bar{1}11]$ channeling map for $YBa_2Cu_3O_x$ showing the dominant bands which were observed in this study. The pattern is for a crystal with its $[\bar{1}11]$ pole parallel to the electron beam and its (110) plane lying horizontally. The speckled regions, such as the zone axis at $[\bar{6}01]$, have been added to emphasize prominent features which proved very helpful in allowing unknown patterns to be identified. There are, of course, many more bands on the actual patterns than shown in Fig. 1, but the bands of Fig. 1 are the dominant bands plus a few which proved useful in identifying patterns. For example, the patterns are nearly symmetrical across the $(1\bar{1}6)$ band above $[\bar{3}31]$ and the $(1\bar{1}3)$ band is helpful in identifying locations in this region. The computer program of Young and Lytton[15] was useful in the construction of Fig. 1, but only as a guide. The use of structure factor calculations to predict the appearance of the map was only partially successful because the relative intensities of several bands was not as predicted. For example, as shown in Fig. 2(a), the (010) band was not resolved whereas the (040) is resolved. The basal plane band appeared somewhat diffuse and was dominated by a single band which corresponded approximately to the predicted d spacing for (006). The (006) band is particularly easy to identify because as seen in Fig. 2(c) it does not display higher-order bands. The $(2\bar{2}6)$ band appeared somewhat sharper than $(1\bar{1}3)$ and produced a characteristic double band quite helpful in identifying patterns.

B. Twin habit plane

The habit plane of the optical twins was confirmed to be {110} by comparing the SACPs from selected grains to the

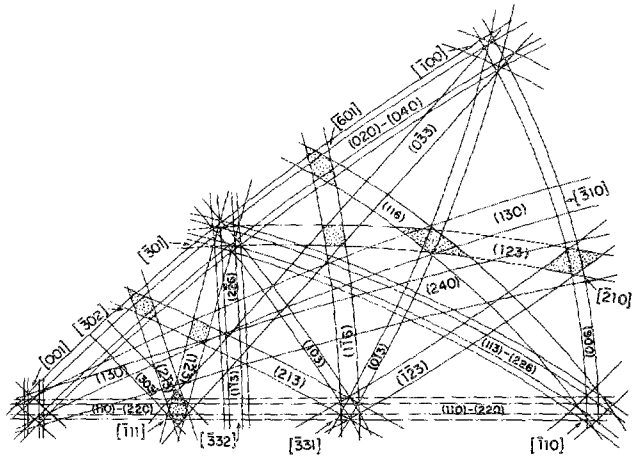


FIG. 1. The dominant bands appearing on a $[\bar{1}11]$ standard triangle channeling map.

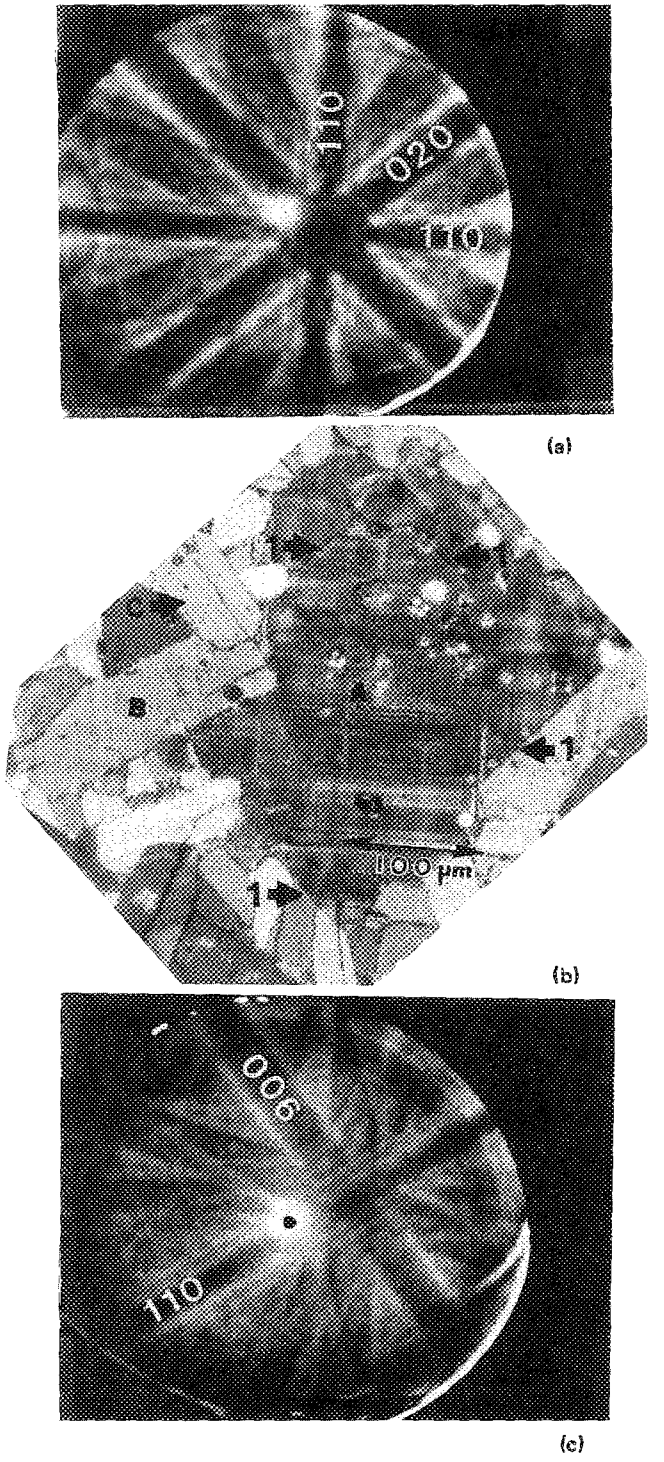


FIG. 2. (a) SACP of grain A, (b) optical image of several grains; oriented with SACPs by the use of the SEM image, and (c) SACP of grain C.

polarized light micrographs of the same grains. The proper orientation of the optical micrographs was found by matching them to images of the polished surface taken in the SEM. It is very important when comparing SEM images to the SEM channeling patterns to be sure that no rotation has occurred between the two due to changes in lens currents. To avoid such effects all SEM images were made by physically lowering the sample without changing lens currents after an SACP was obtained,[16] and realizing that the SACP and SEM images are rotated 180° about the beam relative to each

other.[17] Figure 2(b) shows an optical micrograph of several grains which were examined. The corresponding SACP for grain A is shown as Fig. 2(a) and that for grain C is shown as Fig. 2(c). The {110} planes are identified in Fig. 2 and it is seen that in both cases they lie parallel to the optical twin traces. Thousands of grains have been examined in polarized light optical microscopy and in all cases either one or two parallel sets of twin patterns have been observed but never more than two. This result is consistent with the twin planes lying along the two {110} planes. Grain C is an example where only one set of optical twins is observed. The crystallographic locations of the directions normal to the polish surface for grains A and C are shown on the standard triangle in Fig. 3, where the line segments at each location give the orientation of the {110} twin traces displayed on the SACP.

Grain B is seen to display twin planes crossing at acute angles considerably less than 90° and its location and twins traces are also shown on Fig. 3. For orientations lying along (110) the twin traces should be orthogonal; for orientations in the basal plane the twin traces should be parallel and lie perpendicular to the (006) band, whereas for orientations in the center of the standard triangle the angle between twin traces is expected to become nonorthogonal. The details of the nonorthogonal case are presented elsewhere[18] and this study is limited to grains lying along (110) and (006). For the 12 grains shown on Fig. 3 it is seen that the twin traces lie parallel to {110} in all cases, within our experimental limits, which we estimate as roughly $\pm$ 2°–3°. Grain C is an interesting example because its twin spacing appears unusually large. It may be seen from Fig. 3 that this results because the twin traces observed are for the ($\bar{1}$10) planes, which make an angle of only 4.3° with the polish surface.

C. Habit plane of flat boundaries

It is generally observed that many of the flat sided grains display a large aspect ratio, such as grains B and C of Fig. 2(b). As discussed above, there is TEM evidence[11,12] that the long flat sides of such grains are basal planes. If this is true then if a channeling pattern on such a grain displays a (006) band, the band should lie parallel to the edge of the grain. The (006) band will only appear on the pattern if the *c* axis of the grain lies nearly in the plane of the polish, within $\sim \pm 13°$ for the conditions of the patterns taken here. Grain C of Figs. 2(b) and 2(c) is an example of this case, and by comparing these two figures it is apparent that the grain edge does lie parallel to the (006) band. Similar information may be obtained for grains having their *c* axis at high angles to the surface by locating the SACP on the channeling map for the grain, comparing the pattern to the SEM image, and then plotting the orientation of the long flat boundary on the standard triangle. This has been done for some 22 grains from three different samples on Fig. 4, and it is seen that in all cases the long flat boundary lies parallel to the (006) basal plane band. Although the evidence is a strong indication, it does not prove that the long flat edges are produced by basal plane boundaries because the angle of the grain boundary producing the long flat edge with the polish surface is unknown. A two surface analysis is needed to evaluate the grain boundary angle with the polish surface.

Two surface analyses were done on four grains by fracturing a polished sample and examining the grains along the edge of the polish surface and the fracture surface. Some high aspect ratio grains were observed to fracture along their long flat surface and grain D of Fig. 5 is an example. By rotating the sample about an axis through the fracture edge it was possible to align the fracture surface of the grain parallel to the electron beam so that if the fracture surface were the grain boundary, the grain boundary was aligned parallel to the beam. For a basal plane boundary the corresponding (006) band would then run through the center of the SACP and be parallel to the fracture edge. Point D of Fig. 4 shows that the expected arrangement was obtained for grain D. Point D′ shows the arrangement for grain D in its unrotated position, i.e., with the polish sample surface normal to the electron beam prior to the rotation required to align the fracture edge parallel to the beam. Grain E of Fig. 4 gives the arrangement after rotation for a second grain which also fractured along a long flat edge.

A slightly different technique was used for two surface analyses on high aspect ratio grains which fractured transgranularly across a long flat edge. Because of the large depth

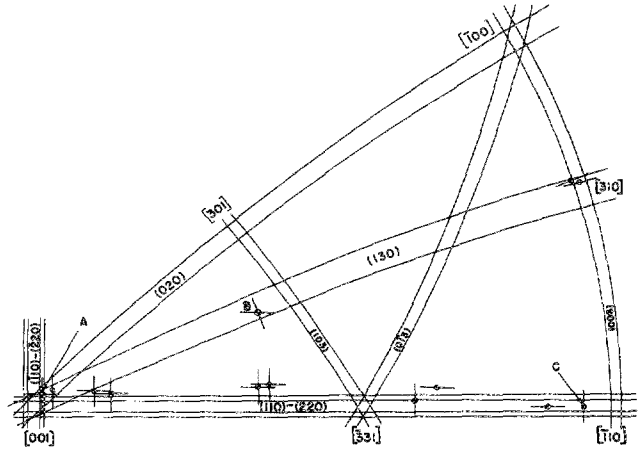


FIG. 3. The circles locate the crystallographic directions of the normals of several grains on the polish surface. The line segments locate the direction of the twin plane traces relative to the pattern.

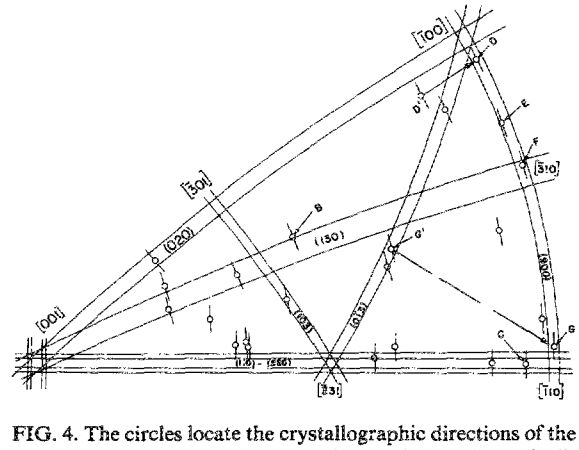


FIG. 4. The circles locate the crystallographic directions of the normals of several high aspect ratio grains on the polished surface. The line segments locate the directions of the long flat boundaries on the polish surface relative to the pattern.

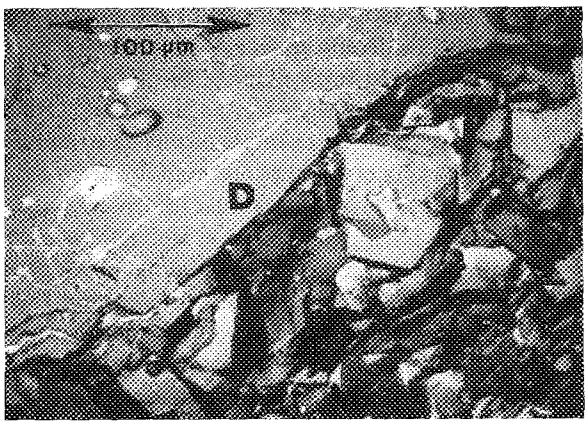
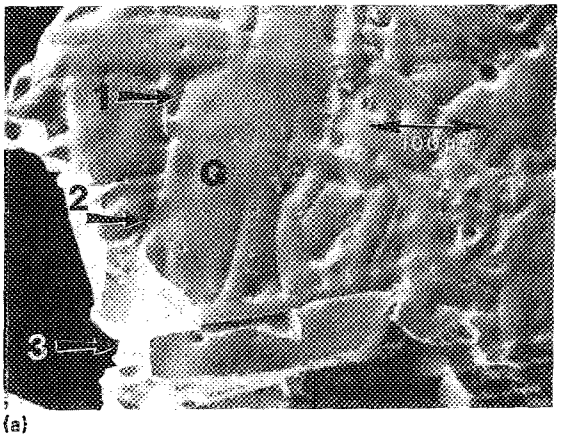
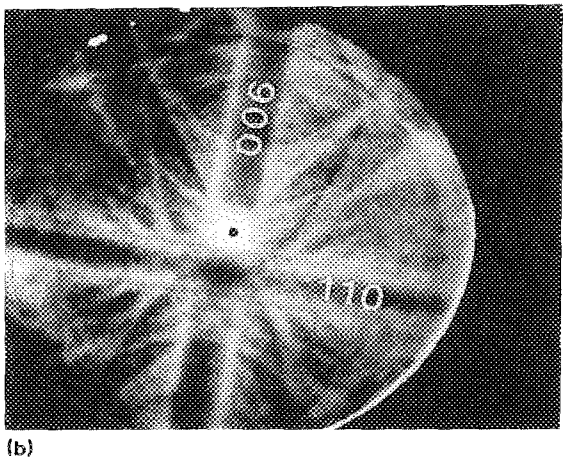


FIG. 5. SEM image of fracture surface showing grain D after sample was rotated to align the fractured face of grain D parallel to the beam.

of resolution of the SEM it is possible to follow the edge of a grain simultaneously along the polish and fracture surfaces. Figure 6(a) shows grain G after alignment to bring its grain boundary along 1–2 parallel to the beam. The long flat edge of grain G extends along the polish surface from 1 to 2 and along the fracture surface from 2 to 3. When the grain boundary is parallel to the beam the line 1-2-3 is a straight line, but when it is not, line segment 1-2 makes an angle with line segment 2-3. Rotation of the sample about an axis parallel to direction 1-2 has produced the proper alignment required to make 1-2 parallel to 2-3. The SACP after rotation is shown as Fig. 6(b) and it is seen that the (006) band lies in the grain boundary plane. The original orientation of grain G prior to rotation is shown on Fig. 4 as G′. Grain F in Fig. 4 shows the orientation of a second transgranular fractured grain after rotation. In conclusion, all four of the high aspect ratio grains examined by two surface analyses, grains D, E, F, and G have been shown to have a basal plane as their long flat grain boundaries. This result plus the additional information of the other 18 grains of Fig. 4 present strong evidence that the long flat surface of all high aspect ratio grains are basal planes.



(a)



(b)

FIG. 6. (a) SEM image of grain G after rotation to align its edge 1-2 parallel to the electron beam. (b) SACP for grain G after rotation.

D. Discussion

All of the patterns examined here are from grains which are composed of packets of fine twin lamellae. This means that the patterns are a superposition of patterns from both twin and parent matrices. In order to investigate what effects might arise from this superposition, the Kikuchi patterns obtained in thin samples in the TEM were examined. These patterns, although produced by different imaging techniques, bear a one-to-one correspondence with channeling patterns, and have the advantages that their resolution is much better and that they may be obtained from regions wholly within one individual twin packet. Patterns were examined from the twin matrix and parent matrix on either side of twin boundaries at several locations in the standard triangle, but in no cases was any obvious difference observed in the two patterns. It is concluded that the 90° rotation about [001] present in the twinning of $YBa_2Cu_3O_x$, coupled with the close match of the a and b lattice parameters produce changes in the patterns too small to be easily detected in either the Kikuchi or the channeling patterns.

In many of the grains examined it was observed that the SACPs used appeared to be a superposition of two or three patterns from subgrains having rotational misalignments on the order of 0.5°. The SACPs used originated from areas of around 20 μm diam. In an effort to see if subboundaries could be located, the scan angle was reduced to around 8° which produced patterns from an area on the order of 2–4 μm. In some grains the doublet patterns were found to remain over large areas of the grain, while in others they disappeared. These results show that many of the large grains examined here contain 0.5°–1° subgrains in the size range of less than 3–20 μm. The origin of these misorientations is unclear. They were present in a large fraction of the grains, roughly 70%. (Patterns from one to two 20 μm diameter areas on 18 of 26 grains showed doublets.) Perhaps the subgrains originate from the tetragonal to orthorhombic transformation which occurs on cooling and also produces the twin structure. Alternately, they may result from rotations due to cracking in these grains. It can be seen in Fig. 2(b) that many of the grains contain cracks, and this was found to be a common feature. The origin of the cracks could well be the anisotropic thermal contraction mentioned above, but the cracking might also be enhanced at the polish surface by the mechanical polishing process, or simply by volume changes associated with the sample reaction with water. We

have found that surface cracks sometimes grown on samples left exposed to air.

Some estimates of the three-dimensional morphology of the grains can be obtained from the present results. It may be noticed that no grains near an [001] orientation are included on Fig. 4. The reason for this is that grains with near [001] orientation were all similar to grain A of Fig. 2(b) in that they did not display a large aspect ratio, but were generally equiaxed on the polish surface. The flat sides of grain A, labeled with 1 on Fig. 2(b), are most likely (100) and (010) faces since these sides lie parallel to the traces of these planes on the figure. Several similarly oriented [001] grains were examined and it was generally found that they were bounded by plane traces along (100), (010), and {110}. It appears likely that the relative grain growth rates in these samples is slowest in the c direction followed next by [100] and [010] directions and finally the two ⟨110⟩ directions. Grain growth occurs at high temperatures where the crystals are tetragonal and the [100] and [010] directions are then equivalent. The net result of this growth rate anisotropy would be grains shaped like a penny, having a faceted edge, the tops and bottoms being basal planes, and the facet planes around the edge being (100), (010), ($\bar{1}$10), and (110) planes. This shape is quite similar to the single crystals which are produced by flux growth, and this result is consistent with evidence[19] which shows that the large grains produced by the present processing technique involve liquid phase sintering. It seems clear that to avoid basal plane boundaries with their undesirable superconducting properties[11] it would be desirable to form the grains in the absence of a liquid phase.

The above argument assumes that the flat faces of the grains arises from the kinetic effect of variation in growth velocity with crystallographic orientation. An alternate explanation would be that a very strong anisotropy exists in the interfacial surface energy of the grain boundaries. It was pointed out to us[20] that this latter effect is probably of secondary importance, however, because as illustrated in Fig. 2(b) the internal pores are consistently found to be spherical shaped. This result means that there is only a small anisotropy in the energy of the surface/vapor interfaces, and it seems likely, therefore, that the anisotropy in the grain boundary interfaces would also be small.

IV. CONCLUSIONS

This study has demonstrated that reasonably sharp electron channeling patterns may be obtained from electropolished $YBa_2Cu_3O_x$ grains. The following conclusions have been established. (a) The dominant bands which appear on the electron channeling map have been determined. (b) It was demonstrated that the optical twin planes lie parallel to the {110} planes. (c) It was demonstrated that the long flat sides of high aspect ratio grains are bounded by basal planes. (d) A majority of the large grains examined here contained 0.5°–1° subgrains, ranging in size from less than 3 to 20 μm. The origin of these subgrains may be due to sample handling.

In addition to the above, the experimental evidence indicates that the dominant grains are shaped like a penny having faceted edges with basal planes bounding the top and bottom. The faceted edge planes consistently lie parallel to the trace of the (010), (100), and {110} planes and are most likely composed of combinations of these planes. Evidence indicates that the anisotropic shape arises mainly from anisotropic growth rates which occur in the liquid phase sintering thought to be dominant in the formation of the large grained samples examined here.

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