The Use of Cubic Nd-Ba-Cu-O Seeds to Create θ[100], 90°-θ[100], and θ[001] Tilt Y-Ba-Cu-O Grain Boundaries

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***Abstract*—Using seeding techniques to control the orientation of grains, we have been able to create a wide variety of $YBa_2Cu_3O_{6+x}$ grain boundaries. In addition to five domain samples with 90°[100] twist and tilt grain boundaries, we have now developed a method to produce grain boundaries in the *same* sample that have the misorientations θ[001] tilt, θ[100] tilt, and 90°-θ[100], where the misorientation angle θ is fully controllable. We will demonstrate how these boundaries can be synthesized, give experimental evidence via polarized light microscopy and electron backscatter patterns (EBSP) that the intended grain boundaries were indeed formed, and discuss the importance of these boundaries in future grain boundary studies.**

I. Introduction

Grain boundary (GB) studies in $YBa_2Cu_3O_{6+x}$ (Y-123) have mainly focused on [001] tilt misorientations, as these are the easiest non-general GB misorientations to fabricate in thin film [1,2,3] and bulk[4,5] forms. Real world conductor applications, however, involve GBs of a number of other types of misorientations. They can range from [001] twist to [100] tilt, to general misorientations, for which the rotation axis may not be a low index crystallographic direction. It is of keen interest to learn if certain types of misorientation axes or grain boundary planes are more favorable to current transport than others. This information can be used to better focus the key alignment parameters for conductor fabrication.

The effect of the grain boundary plane has been discussed in a number of reports[6,7,8]. In this report, we will describe a fabrication technique that allows us to explore the role of the rotation axis on superconducting properties. Specifically, we synthesize samples that not only contain a [001] tilt grain boundary of some pre-selected misorientation angle θ, but a [100] tilt grain boundary of that same θ, and an additional [100] tilt grain boundary of 90°-θ. It is important to note that due to symmetry the maximum misorientation generally discussed for [001] tilt type GBs is 45°, as the samples are twinned and Y-123 is approximated as tetragonal (a~b). Thus if we plotted normalized J_c vs. θ up to 90° for [001] tilt type grain boundaries, the symmetry would result in a reflection in J_c values about θ=45°. For [100] tilt type GBs, the maximum in non-symmetric misorientation is 90°. However, except for the special case of 90°[100] tilt [4,7,9], [100] tilt GBs have only been explored up to θ=21°[6]. It would be interesting to plot [100] tilt data as a function of θ, as reports indicate that 90°[100] tilt GBs may be junction-like[9,10] and so a reflection in $J_c(\theta)$ about θ=45° would not be expected. This is reasonable based on the symmetry of the Y-123 unit cell.

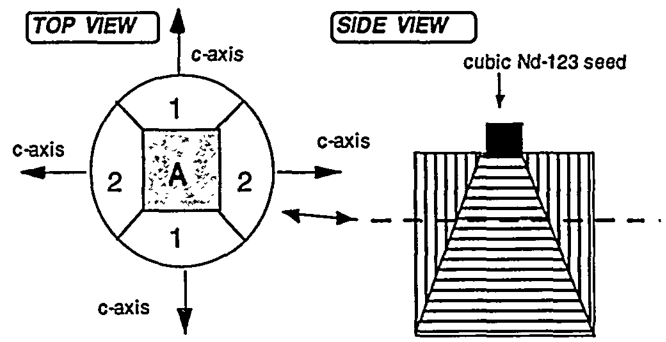

Fig. 1. A single cubic Nd-123 seed generates 5 domains in the Y-123 pellet, with 3 symmetrically unique orientations misoriented 90° from each other.

It has been demonstrated previously that cubic Nd-123 (actual composition at surface: $Nd_{1.25}Ba_{1.75}Cu_{2.6}Al_{0.4}O_x$[11]) seeds can be used to create five domain Y-123 samples, wherein the five domains are misoriented 90° from each other[12]. In an ideal five domain sample, as in **Fig. 1**, the center domain (in this paper labeled "A") grows with the c-axis parallel to the vertical direction of the cylindrical pellet, while the other four domains grow with the c-axis parallel to the radius of the pellet (labeled "1" or "2", and the other two domains misoriented 180° are degenerate). Combining this concept with the dual seeding concept[5] of creating [001] tilt bicrystals, a variety of grain boundaries should be formed. From **Fig. 2a** we see that with dual cubic seeds and perfectly straight grain boundaries, the only [100] tilt GBs that can be formed are of angle θ that is equal to the misorientation of domains A and A′ (dictated by the placement of the seeds). However if the GB macroscopically facets (**Fig. 2b**), we may find regions where 1-2′ or 2-1′ intersect, forming 90°-θ [100] tilt grain boundaries. As the center c-axis normal domains (A and A′) grow in a pyramidal shape, they will eventually touch at some distance vertically from the top of the pellet, forming the [001] tilt GBs like those formed by flat Nd-123 seeds[5].

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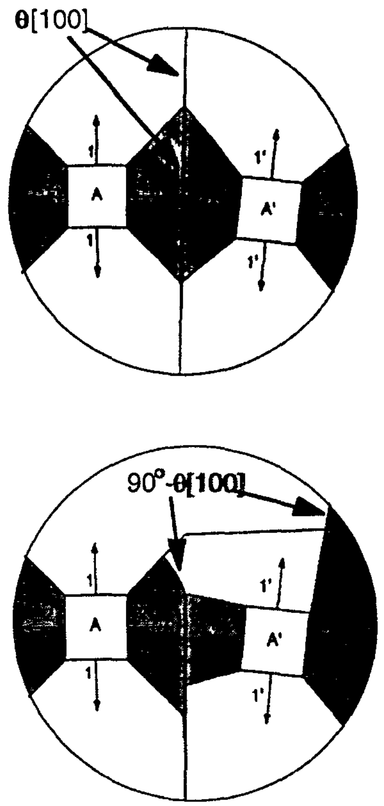

Fig. 2. The regions A and A′ represent the c-axis normal regions grown from the Nd-123 seeds, and the numbered regions all have c-axis in the plane of the paper in the direction of their arrow. When the A and A′ regions are misoriented by θ and with straight grain boundaries, as in a) they form θ[100] GBs at intersections of regions 1-1′ or 2-2′. If the grain boundaries macroscopically facet such that they separate regions 1-2′ or 2-1′, as in b) a 90°-θ[100] grain boundary is formed. When regions A and A′ growth together vertically lower in the pellet, a θ[001] tilt grain boundary is formed (not shown in this figure).

II. Experimental

Cubic Nd-123 seeds were grown as described in [12],[10]. Some cubic seeds were ground and polished, to reveal the actual domain structure of the seed. A commercial mix of 75% Y-123 and 25% Y_2BaCuO_5 (211) with a small amount of Pt is pressed into 5mm diameter pellets approximately 6mm tall. The seeds were placed upon the top surface of the 123 mix pellet and aligned to the appropriate θ using tweezers viewed through a light microscope. The angle θ is measure by using the circular rotating stage of the light microscope and aligning the eyepiece reticule with the 90° corners of the seeds (**Fig. 3a**). The data described in this paper is for a sample in which the seeds were misaligned by ~43°. The assembly is placed in an alumina crucible buffered with 211 and carefully placed in a vertical tube furnace. A traditional melt-texture program is run[13], with the key growth step being the slow cool through the peritectic from 1000°C to 930° at 1°C/hr. This is when the Y-123 domains grow from the template defined by the domains in the Nd123 seeds. As the samples are grown in air, a subsequent oxygenation step is performed after growth in tube furnace under 99.99% pure flowing oxygen. Macro photographs are taken of the sample surface to notice the post-melt texture misorientation of the seeds (**Fig. 3b**). Samples are then cut with a diamond saw along the radius of the pellet, yielding several discs per pellet. As the growth of the c-axis domain is pyramidal, most of the interesting boundaries are towards the top 1/3 of the sample. Samples are then ground flat with 600 grit SiC paper and polished with 3μm alumina paper, and, if necessary, 0.3μm suspensions of aluminum oxide in methanol on a nylon pad. The samples are then view under a polarized light microscope to reveal grain boundary contrast. Images of the various domains are captured with a digital camera and the entire image of a 5mm diameter sample slice can be assembled. From these polarized light micrographs and knowledge of the seed misorientation, general conclusions about the misorientation angle and type of various GBs can be inferred. To verify the misorientation angles, the samples are etched in a 1%HBr in ethanol solution for approximately 45 seconds (to reveal an undamaged surface) in preparation for electron backscatter patterns (EBSP). The EBSP patterns are created by secondary electrons reflected from an electron beam in a scanning electron microscope, and the unique Kikuchi patterns reveal the precise misorientation to ~1° for areas as small as 0.2μm[14]. Software analysis was used to index the patterns based on the known crystal structure to obtain the misorientation between the two regions.

a) b)

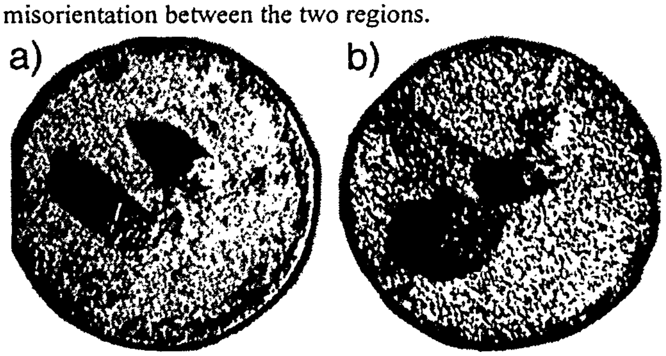

Fig. 3. a) Two cubic seeds are placed at a misorientation angle θ on the surface of a Y-123 pellet before melt-texturing. b) After melt texturing the angle between the seeds is re-recorded. (Dimensions: pellet diameter = 5mm)

III. Results

The polarized light micrograph of the dual cubic seed sample is shown in **Fig. 4**. The large misorientations between the domains appears as reflected polarized light contrast. The imperfect grain boundary plane growth allowed a small region of 90°-θ[100] GB as well as larger regions of θ[100] GBs. The central domains, labeled A and A′, with the c axis normal to the sample surface can be easily identified even without the use of twin patterns or polarized light contrast. They are marked by a relatively rough surface quality and absence of cracking. In contrast, the c-axis in the plane of the sample can be identified by a relatively smooth surface with cracks along the ab planes. A cause of non-perfect growth is illustrated in **Fig. 5**, where an incomplete seed, in this case a missing lower domain, resulted in the Y-123 center domain growing where the lower, c-axis in-the-plane domain would have been.

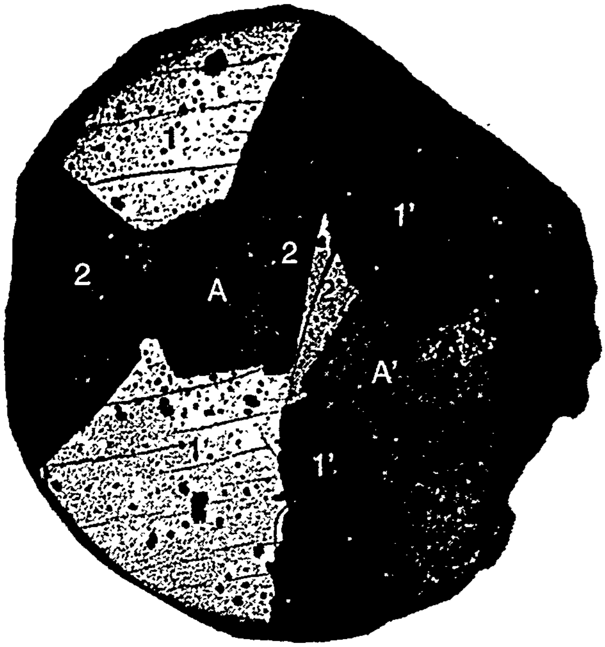

Fig. 4. A dual cubic seed sample where the seeds were placed 45° in rotation. Note that the boundary planes are not perfect, allowing for a region of 2-1′ (90°-θ[100]) contact as well as 1-1′ or 2-2′ (θ[100]). Also note that due to imperfect seeds, regions A and A′ can extend beyond the roughly square shape of the seed. (disc diameter 5mm)

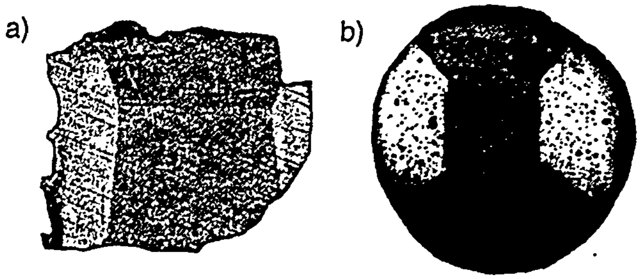

Fig. 5. An imperfect Nd123 seed (dimension ~ 1 mm) in a), in this case a missing lower domain, results in the growth pattern in b), where the c-axis normal domain spreads from the center to the region where the missing domain would have grown. (disc diameter 5mm)

Fig. 6 shows the Kikuchi patterns from representative areas in grain A and A′. As the difference in patterns can be quite subtle, high quality patterns are required to obtain a positive identification of the orientation. Subtle differences in the patterns, such as the distance between parallel bands and the number of bands intersecting at a location help to define the sample orientation. Patterns were taken as close to the θ[100] and 90°-θ[100] GBs as possible. **TABLE 1** summarizes the range of experimental data; an approximated value for the angle and axis pair was obtained by taking a median value for the rotation angle and noting the low index axis the data had in common. The θ[001], θ[100] and 90°-θ[100] values are roughly obtained as predicted. A slightly lower misorientation angle for the 90°-θ might be expected, but besides an experimental error of ~1°, the slight mosaic spread in melt-textured material can change the value from the predicted by a few degrees[15].

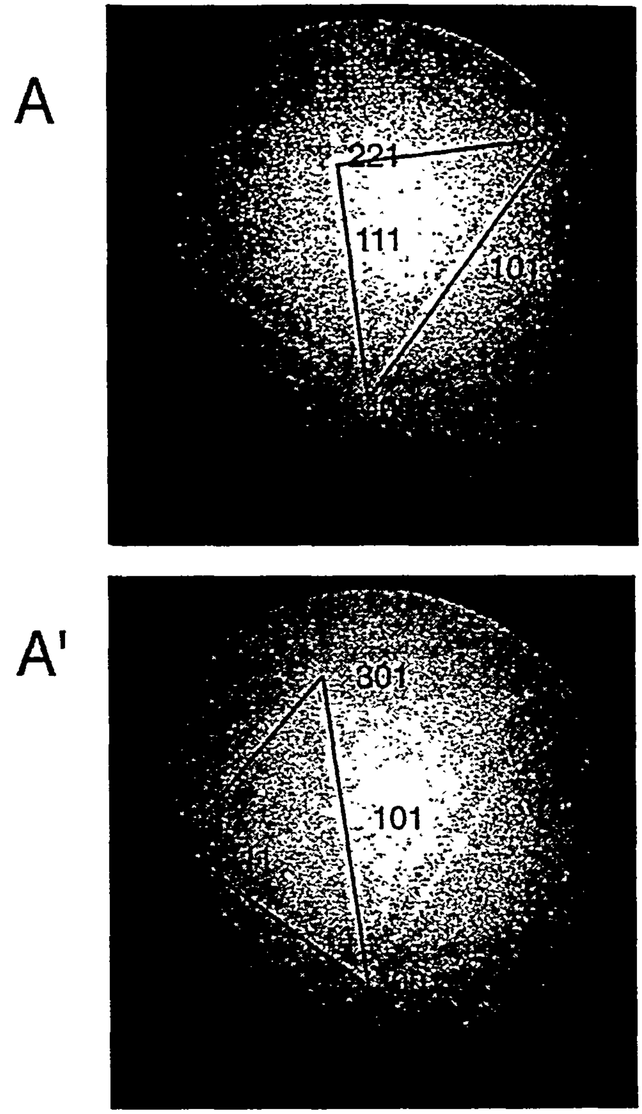

Fig. 6. Kikuchi Backscatter patterns from regions in grain A and grain A′. The 001 is easily recognizable by three intersecting bands of high contrast. The rotation is noted by highlighting the triangle between the [001], [221] and [301] directions; the relationship between A-A′ is ~43°[001].

TABLE 1

Regions	actual θ/axis range	approx. θ/axis
A-A′	41°[1 1 9] - 44°[1 0 9]	42.5°[001]
2-1′	41.4°[$\overline{12}$ $\overline{1}$ 1] - 42.6°[7 $\overline{81}$ 5]	42.0°[100]
2-2′	47.5°[$\overline{3}$ $\overline{84}$ 1] - 49.5°[$\overline{25}$ $\overline{1}$ 1]	48.5°[100]

IV. DISCUSSION

The GB misorientation angles have matched the predicted values to within a few degrees, reasonable considering the mosaic nature of melt-textured Y-123. We have found that imperfect cubic Nd-123 seeds and growth development actually can help extend the range of boundaries that can be grown. Slight mosaic spreads of a few degrees are beneficial as well, as small essentially homogeneous regions can be isolated for transport via laser cutting[8], but the larger boundary region as a whole allows a small spread of misorientations to investigate within one sample. The identification of imperfect seeds before growth can be used for more predictable control what grain boundaries will be grown.

V. CONCLUSION

We conclude that the dual cubic seed technique allows us to create samples for the purpose of probing the effect of the rotation axis on transport properties in bulk Y-123, specifically the [100] vs. [001] rotation axis. From the same set of samples we can as well as get a range of samples to create a [100] tilt, 0-90° vs. J_c plot if the proper seeds are chosen.

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