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**INDUCING SELF-ASSEMBLY OF Y_2BaCuO_5
NANOPARTICLES VIA Ca-DOPING FOR IMPROVED
PINNING IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (POSTPRINT)**

Paul N. Barnes, T.J. Haugan, and S. Sathiraju

**Mechanical Energy Conversion Branch
Energy/Power/Thermal Division**

F.J. Baca

University of Kansas

C.V. Varanasi

University of Dayton Research Institute

R. Wheeler and F. Meisenkothen

UES, Inc.

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Inducing self-assembly of Y_2BaCuO_5 nanoparticles via Ca-doping for improved pinning in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

P.N. Barnes^{a,*}, T.J. Haugan^a, F.J. Baca^{a,b}, C.V. Varanasi^{a,c}, R. Wheeler^d, F. Meisenkothen^d, S. Sathiraju^a

^a Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, OH 45433, USA

^b Department of Physics and Astronomy, University of Kansas, Lawrence, KS 66045, USA

^c University of Dayton Research Institute, Metals and Ceramics, 2645 Fifth Street, Dayton, OH 45469, USA

^d UES, Inc., 4401 Dayton-Xenia Drive, Dayton, OH 45432, USA

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ABSTRACT

Different mechanisms may exist as a means to provide additional or specialized enhancement of existing nanoparticle pinning in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) thin films. In the particular case of Y_2BaCuO_5 (Y211) nanoparticles, Ca-doping of these nanoparticles via addition to the Y211 target material provides an additional increase to the $J_c(H)$. YBCO + Y211 samples were created by pulsed laser deposition with alternating targets of YBCO with Y211 and Y211 doped with Ca. Initial indications suggest that this improvement in pinning results from some scattered short-ranged self-assembly of the nanoparticles into short nanocolumns.

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1. Introduction

Significant progress has been made on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO or Y123) superconductors with respect to its application as a high temperature superconducting (HTS) wire [1,2]. With this, an emphasis for its successful deployment, among others, is on improvement in the magnetic flux pinning properties [3,4]. Most methods of pinning enhancement, regardless of the particular means of creating the pinning center, are largely dependent on the geometry of the particular pinning centers in the high temperature superconducting (HTS) film. Initially, a nanoparticle dispersion of non-superconducting additions was demonstrated to improve the critical current density (J_c) in YBCO and can potentially provide an isotropic pinning enhancement for the superconductor [5–8]. The nanorod/nanocolumnar pinning centers created by the addition of BaZrO_3 (BZO) or BaSnO_3 (BSO) or the more recent RE_3TaO_7 (RTO), RE = rare earth, provide columnar pinning that tends to preferentially provide enhancement in the c -axis direction, but still provides overall angular improvement [9–15].

Although these nanoparticle and nanocolumnar pinning additions provide the expected enhancements due to their particular type of geometric inclusion, it does not account for the total nature of their pinning. For example, it is known that chemical interactions between the doping additions and the superconductor can lower the T_c of the superconductor causing degradation of the performance. This can limit the utility of some additions such as BZO where excessive amounts heavily degrade the J_c in these samples [16]. Others can be more forgiving such as BSO or RTO [15,17]. Even so, the large improvements in YBCO when the applied field is perpendicular to the face of the films ($H \parallel c$) are largely due to the self-assembly of the added BZO, BSO, RTO, etc. pinning material into nanorods and/or nanocolumns within the YBCO matrix. Since Y211 when added to the YBCO provides improved pinning for $H \parallel c$ even though it tends not to self-assemble, it could potentially provide an even larger improvement if the nanoparticles could be “encouraged” to self-assemble into nanocolumnar structures.

A critical question, however, is whether this additional improvement can be made by some simple modification. Research has already demonstrated that the addition of Y211 as a nanoparticle dispersion in YBCO can effectively enhance its pinning properties [5,18,19]. The focus of this paper is to point out how self-assembly of the Y211 nanoparticles can be accomplished

* Corresponding author. Tel.: +1 937 255 4410; fax: +1 937 255 4307.

E-mail address: paul.barnes@wpafb.af.mil (P.N. Barnes).

through the doping by Ca of the Y211 target material leading to an even greater enhancement of the pinning in YBCO + Y211 samples. Doping of Ca at the Y site in YBCO films has been studied extensively by many researcher as Ca is expected to increase the population of holes in YBCO by replacing Y^{+3} with Ca^{+2} hence improving superconductor coupling between the grains [20–23]. Hammerl et al. have reported a 3 to 6-fold improvement of J_c for annealed YBCO/Ca-doped YBCO multilayer films [21]. Daniels et al. have reported that Ca-doping increased the intergrain J_c in spite of a lower T_c in the higher concentrations of Ca-doped YBCO films [22]. Considering these factors, it seems reasonable to introduce Ca-doped Y211 pinning as a combination effect of Ca-doping (by diffusion) as well as the Y211 pinning in YBCO thin films, even if self-assembly of the Y211 did not occur. However, the effects of Ca-doped Y211 nanoparticles on grain boundaries, via bicrystals, is reported elsewhere and not the subject here [24,25]. The results presented here is the effect of the Ca-doped Y211 on YBCO films deposited on single crystal substrates.

2. Experimental

Flux pinning is studied in YBCO thin films deposited by pulsed laser deposition (PLD). Details of the film deposition conditions and process parameters are given elsewhere [17,18]. For Ca-doped $Y_{2-x}Ca_xBaCuO_5$ (Y211) nanoparticle additions, PLD targets were made by solid-state reaction starting with high purity Y_2O_3 , $BaCO_3$, CuO , and $CaCO_3$ finely ground together in appropriate stoichiometric ratio of $Y_{1.9}Ca_{0.1}BaCuO_5$ (5 at.% Ca-doped Y211) and $Y_{1.8}Ca_{0.2}BaCuO_5$ (10 at.% Ca-doped Y211). These powders were reacted and formed into targets of dimensions 2.54 cm (1 inch) diameter and 1.5 cm thick, using the standard solid-state sintering methods. To understand the doping effect of Ca in the Y211 nanoparticulate structure, we have deposited YBCO films with and without nanoparticulates of Ca-doped Y211 in addition to YBCO films with plain Y211 nanoparticles. Polished $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) (1 0 0) substrates were used for growth of the films. Deposition parameters included a KrF laser $\lambda = 248$ nm wavelength, $3 J/cm^2$ laser fluence, 25 ns pulse length, and 4 Hz laser repetition rate. A post-deposition anneal was conducted for the films at 500 °C and 1 atmosphere of oxygen. Film thicknesses were in the range of 0.2–0.3 μm .

The superconducting transition temperature (T_c) was measured using an AC susceptibility technique with the amplitude of the magnetic sensing field strength, h , varied from 0.025 to 2.2 Oe, at a sensing frequency of approximately 4 kHz. Magnetic J_c measurements were made with a vibrating sample magnetometer (VSM) in magnetic field strengths of 0–9 T, and a ramp rate of 0.01 ($T s^{-1}$). The J_c of the square-shaped samples was estimated using a simplified Bean model $J_c = 15 \Delta M/R$, where M is the magnetization/volume from M–H loops, and R is the radius of volume interaction. Scanning electron micrographs were taken with FEI Sirion High Resolution Microscope in ultra-high resolution mode using a through-lens-detector (TLD), with magnifications up to 100 k $\times$. To study the microstructural properties by transmission electron microscopy (TEM), cross sections were prepared using focused ion beam systems. TEM Micrographs were taken using a Phillips CM-200 with a field-emission source operating at 200 kV. Films were also characterized using X-ray diffraction.

3. Results and discussion

Since the orientation of the Y211 material in the YBCO has not yet been reported, this was considered first. To examine this, a zone-axis selected area diffraction pattern (SAD) was collected, with the e-beam directed perpendicular to the growth direction of the YBCO film (Y123 phase). The SAD pattern contains

reflections from both the Y123 phase and the Y211 phase. Fig. 1 shows this zone axis pattern, along with phase identification and indexing information which is given in Table 1. It should be noted that the orientation of the Y211 is not random in the YBCO matrix. The diffraction information not only shows the Y211 phase is present, but has an orientation relationship within the matrix of $(001)_{123} \parallel (001)_{211}$ and $[010]_{123} \parallel [100]_{211}$, showing that the nanoparticles form epitaxially, although rotated about the current-carrying Cu–O planes. The lattice parameters measured for the 211-phase are approximately within 5% of the reported XRD values for the phase. Given that the average Y211 nanoparticle size is ~ 10 nm, the lattice distortion is likely a result of the lattice strain induced by the lattice parameter mismatch between the Y123 and the Y211 phases.

It is well-known that Ca-doping in the bulk YBCO degrades the intragranular current density [26]. Ca-doping is employed as a trade-off or balancing of the intergranular and intragranular current density to provide the maximum net overall critical current (I_c) of the material. Based on this, it may be expected that a slight decline could occur in these type of samples, but this is clearly not the case. Fig. 2 shows that the addition of Ca to the Y211 material inclusion provides an additional enhancement over and above that

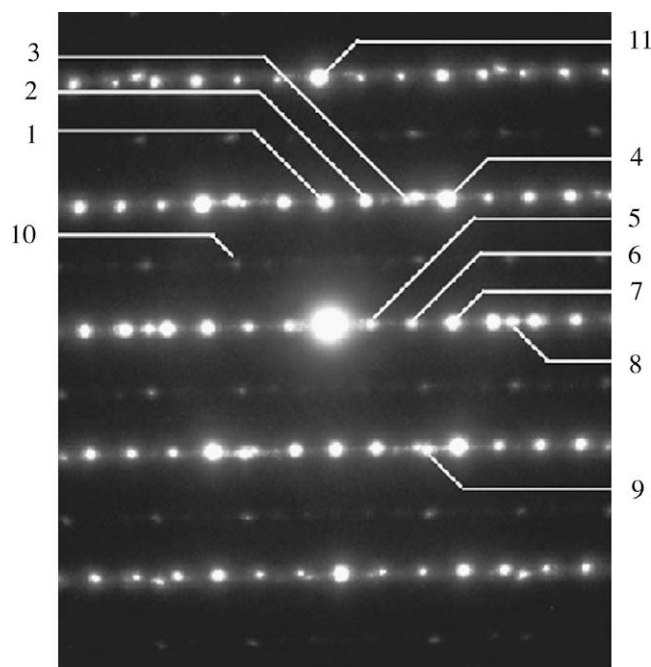


Fig. 1. Selected area diffraction pattern, 123-YBCO [100] zone axis pattern. Electron diffraction pattern taken parallel to the substrate/thin film interface.

Table 1

Pattern reflections with corresponding phase identification and indexing. Orientation relationship is $(001)_{123} \parallel (001)_{211}$, $[010]_{123} \parallel [100]_{211}$.

Reflection	<i>D</i> (mm)	<i>R</i> (mm)	θ (rad)	<i>d</i> (Å)	Phase ID	Index
1	8.4	4.20	0.0032	3.9	123	010
2	8.8	4.40	0.0034	3.7	123	011
3	9.9	4.95	0.0038	3.3	123	021
4	11.8	5.90	0.0045	2.8	123	031
5	2.8	1.40	0.0011	11.7	123	010
6	5.6	2.80	0.0021	5.8	123	020
7	8.4	4.20	0.0032	3.9	123	030
8	12.3	6.15	0.0047	2.7	211	002
9	10.5	5.25	0.0040	3.1	211	201
10	7.5	3.75	0.0029	4.4	211	101
11	16.8	8.40	0.0064	1.9	123/211	020/400

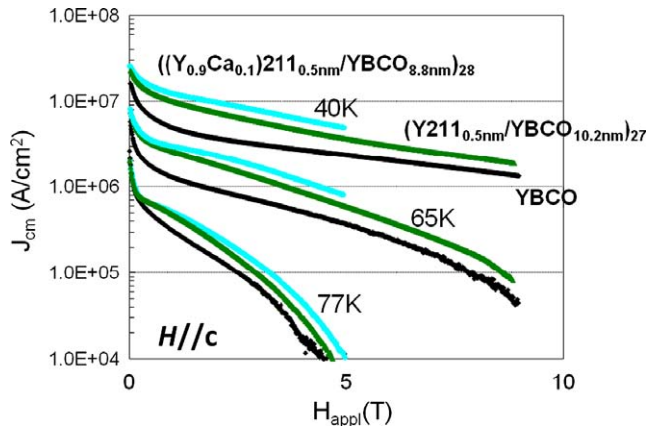


Fig. 2. Magnetization $J_c(H)$ for three different temperatures. Each curve set for the different temperatures are from top to bottom: Ca-doped Y211 nanoparticles in YBCO, Y211 nanoparticles in YBCO and plain YBCO. These depositions were carried out at 800 °C.

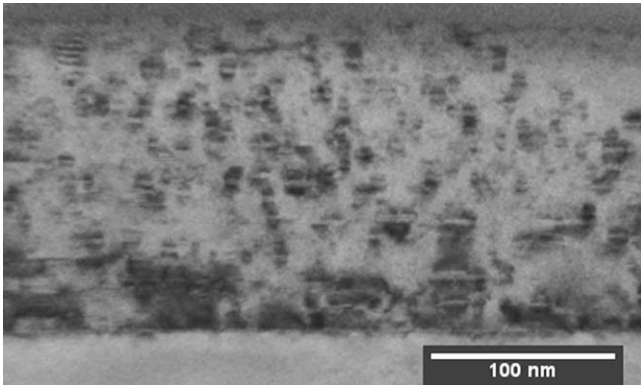


Fig. 3. Cross-sectional TEM image of a Ca-doped Y211 nanoparticle in YBCO multilayer made with $(Y_{0.9}Ca_{0.1})_2BaCuO_5$, a 10% Ca-doping concentration.

of the plain Y211 nanoparticle pinning. This enhancement is maintained at various temperatures from 40 K to 77 K, and the full range of applied magnetic fields studied, $H > 0.1$ T.

Examination of the material inclusion by TEM suggests that the Ca-doped Y211 phase not only forms into nanoparticles, but is beginning to self-assemble itself, as shown in Fig. 3 which is representative of the Ca-doped Y211 pinned YBCO. This self-assembly is not complete, with nanoparticles still present and most of the self-assembly resulting in short nanorods as opposed to complete nanocolumns extending the length of the films. Fig. 4 provides TEM images for Y211 pinned YBCO with no Ca-doping. Fig. 4a is typical of most films regardless of the various deposition parameters used. Some self-assembly did occasionally occur in the plain Y211-pinned films, but not often being only in limited locations. Fig. 4b provides an example of this and perhaps captures the most extensive self-assembled section of the entire sample.

It should also be noted that the nanorods are not stringently aligned in a particular direction. They are generally aligned in the c -axis direction as opposed to the ab -planes, but there is a fairly wide angular range for this growth. Exactly why the addition of Ca to the Y211 nanoparticles will cause this to happen is unknown. Even though it is not perfectly clear why self-assembly is initiated with the addition of Ca-doped Y211, it does indicate the altering the composition of the non-superconducting pinning addition can provide an additional enhancement. With this improvement due to partial self-assembly of the nanoparticles, it can potentially be quite an effective improvement to nanoparticle dispersions by providing mixtures of nanorods and nanoparticles, as well as a more random alignment of the nanorods, for a “best” overall increase with respect to angular performance. Additional research is required to investigate this.

4. Summary

In conclusion, this paper addressed a means to provide additional enhancement to the existing Y211 nanoparticle pinning in YBCO thin films. In this case, Ca-doping of the nanoparticle (via the addition of Ca to the pinning-material target) provides an additional boost to the $J_c(H)$. Initial data was provided that the Ca-doping is causing the Y211 nanoparticles to self-assemble into short nanocolumns or nanorods. Future investigations could be made to determine the angular dependence of the Ca-doped Y211 pinned YBCO since it leads to a mixture of nanorod and nanoparticles which may provide an overall better isotropic pinning effect. This research does not necessarily mean that Ca-doping of all material inclusions will provide enhancement.

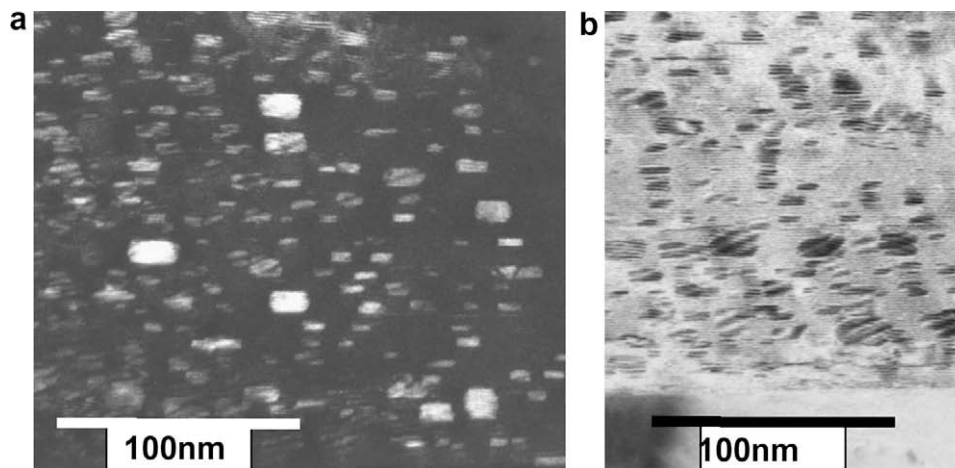


Fig. 4. Cross-sectional TEM image of plain Y211 nanoparticle dispersions in YBCO multilayer: (a) dark-field image of typical Y211 pinned YBCO films and (b) a bright-field image showing a particular section in one sample where some self-assembly did occur without Ca-doping. However, this is uncommon and other parts of the film display the typical nanoparticle dispersion with no self-assembly.

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