Comparison study of the flux pinning enhancement of YBCO superconductor with BZO and BZO + Y$_2$O$_3$ mixed phase additions

M A Sebastian$^{1,2}$, C Ebbing$^2$, W Zhang$^{3,4}$, J Huang$^{3,4}$, H Wang$^{3,4}$, S Chen$^5$, B Gautum$^2$, J Wu$^5$ and T Haugan$^1$

$^1$ U.S. Air Force Research Laboratory, Aerospace Systems Directorate, WPAFB, OH 45433 USA
$^2$ UDRI, University of Dayton, OH 45469 USA
$^3$ Materials Science and Engineering Program, Texas A&M, College Station, TX 77843 USA
$^4$ School of Materials Engineering, Purdue University, West Lafayette, IN 47907 USA
$^5$ Department of Physics & Astronomy, the University of Kansas, Lawrence, Kansas 66045, USA
$^6$ Author to whom correspondence should be addressed: sebastianm1@udayton.edu
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Abstract. Adding nanophase defects to YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) superconductor thin films is well-known to enhance flux pinning, resulting in an increase in current density ($J_{ct}$). While many previous studies focused on single phase additions, the addition of several phases simultaneously shows promise in improving current density by combining different pinning mechanisms. This paper compares the effect of the addition of two insulating, nonreactive phases of barium zirconium oxide (BZO) and yttrium oxide Y$_2$O$_3$, both as a single addition of BZO and as a double addition in conjunction with Y$_2$O$_3$. Processing parameters vary the target composition volume percent of BZO from 2-6 vol. %, while maintaining 3 vol. % Y$_2$O$_3$, and the remaining vol. % YBCO. Pulsed laser deposition produced thin films on LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) substrates at various deposition temperatures. Comparison of strong and weak flux pinning mechanisms, current densities, critical temperatures, and microstructures of the resulting films will be presented. Films produced from the 2 vol. % BZO + 3 vol. Y$_2$O$_3$ doped YBCO target at a deposition temperature of 825 °C attained the highest current density. The addition of second phase Y$_2$O$_3$ impacted the film microstructure, resulting in more isotropic behavior when compared to the YBCO films doped with only BZO.
1. Introduction
Addition of nano-sized insulating phases to YBa2Cu3O7-δ (YBCO) thin films enhances flux pinning, resulting in higher current densities. Previous research has focused on combining the artificial pinning centers resulting from BZO nanorods [1], [2], [3] and Y2O3 nanoparticles [4]. Liu utilized a 1.5 vol. % BZO and YBCO target to produce films on LAO decorated with Y2O3 nano-islands [5]. Optimization of film thickness for films consisting of YBCO with BZO and Y2O3 has also been studied, utilizing a 5 mol. % BZO and 5 mol. % Y2O3 target [6]. It is hypothesized that the combination of BZO and Y2O3 with YBCO influences the lattice strain in the film. This research seeks to explore the effects on current density of doping a YBCO target with 2, 4, and 6 volume percent BZO along with 3 vol. percent Y2O3, with the remaining volume percent YBCO.

2. Experimental Procedures
2.1. Target Preparation
Targets were produced via solid state processing of commercial powders of YBCO, BaZrO3, and Y2O3, which were dried in a box furnace for 8 hours at 450 °C. The dried powders were measured and mixed with an agate mortar and pestle to comprise compositions listed in Table 1. The mixtures were then individually pressed utilizing a Carver die press with 1.25 inch and 1.125 inch diameter dies and a pressure of 6.89 MPa. The targets were then sintered at 850 °C for 60 hours and 920 °C for 156 hours. Final densities of the three targets ranged between 86% and 93%. A YBCO - only target was prepared by similar conditions, with final density 93%.

| Target | YBCO Volume % | BZO Volume % | Y2O3 Volume % |
|--------|----------------|---------------|----------------|
| TS199  | 100.0          | 2.0           |                |
| TS196  | 98.0           | 2.0           |                |
| TS201  | 95.0           | 2.0           | 3.0            |
| TS202  | 93.0           | 4.0           | 3.0            |
| TS203  | 91.0           | 6.0           | 3.0            |

2.2. Thin Film Production via Pulsed Laser Deposition (PLD)
Thin films were produced using pulsed laser deposition (PLD) on SrTiO3 (STO) single crystal substrates, having dimensions of 3.2 mm × 3.2 mm × 0.5 mm and 4.0 mm × 10.0 mm × 0.5 mm. Substrates were cleaned via an ultrasonic cleaner for five minutes with acetone, followed by five minutes with isopropyl alcohol. The substrates were mounted to a YBCO coated heater block with colloidal silver paint. Films were produced via PLD with a Lambda Physik LPX 300 Eximer KrF laser using an energy of 450 mJ, a repetition rate of 8Hz, and a 40Pa O2 atmosphere, followed by annealing at 500 °C in an O2 atmosphere for 30 minutes.

2.3. Film Characterization
Film thicknesses were determined by etching the thin films with nitric acid and measuring the step thickness with a KLA Tencor D-120. Resulting film thicknesses were 290, 247, and 256 nm for the 2, 4, and 6 vol. % double doped BZO + Y2O3, respectively. Single doped BZO films were 135 nm thick. Magnetic current density (Jc,0) and critical transition temperature (Tc) were measured with a Quantum Design Physical Properties Measurement System (PPMS) with a vibrating sample magnetometer (VSM) probe. The VSM data was attained for conditions of 77 K, 65 K, 20 K, and 5 K with an applied field varied from 0-9 T for H // c-axis of the films. Tc,onset temperatures of the films were attained from zero-field-cooled measurements. The measured magnetic data was used to determine the current densities by utilizing a simplified form or the Bean Critical State Model [7,8,9]. Transport current density measurements were conducted through collaboration with Dr. Judy Wu’s research group at University of Kansas. Silver contacts were sputtered through a metal shadow mask on the films, to reduce the...
contact resistance to the microbridges. Microbridges of ≈ 20 µm width and ≈500 µm length were patterned utilizing photolithography. Film surfaces were spin coated with 351 photoresist, exposed at 500W UV for 70 s., developed for 50 s., followed by etching for 2 min. with 0.05% HNO₃. Platinum wires were attached to the microbridges with indium for the electrical connections. A Keithley 2430 1KW pulsed current source meter and HP 34420 nanovoltmeter were used to attain the transport current density. LabVIEW was used to control the increasing amplitude of the current pulse train and synchronize the resulting voltage detected across the film. A short 50 ms pulse width and a long time interval of 3000 – 4000 ms minimized heating. The current density was determined using a 1 µV/cm criteria. A Quantum Design Evercool II Physical Property Measurement System (PPMS) was employed to measure the transport current density as a function of temperature, magnetic field (0-9T), and angle θ between the field and the c-axis of the film, maintaining the field perpendicular to the current. Transport current densities were measured at θ = 0˚ (corresponding to $H_{//c}$), 45˚, and 90˚ (corresponding to $H_{//ab}$).

A FEI Sirion Scanning Electron Microscope (SEM) with ultra-high resolution at 5 kV and a spot size of 3 was used to obtain images of the films’ surface. Cross-sectional Transmission Electron Microscopy (XTEM) images and Scanning Transmission Electron Microscopy image (STEM) were obtained using a FEI Tecnai F20 analytical microscope under the acceleration voltage of 200KV. TEM work was courtesy of H. Wang’s group previously located at Texas A & M University, and currently located at Purdue University. Lattice parameters were determined by x-ray diffraction analysis utilizing the Bruker D8 Discover diffractometer with the following operation conditions: high resolution, Cu tube 1.5418 Å, Power: 40kV, 40mA; 2T: 5-70˚; rocking curves for YBCO (005).

3. Results and Discussion
The experimental results in figure 1 and figure 2 show the resulting current densities verses applied field at 77, 65, 20, and 5K for YBCO films with varying 2, 4, and 6 volume percent BZO and 3 volume percent Y₂O₃ at two different deposition temperatures of 825°C and 810°C. Looking at figure 2, the 2 vol. % double doped BZO films (810 °C deposition temperature) attained a higher current density than YBCO films at 65K, but not at the lower temperatures of 20 and 5K. In contrast in figure 1, the 2 vol. % BZO double doped films grown at 825 °C attained higher current densities than YBCO at both high and low temperatures. Comparing these graphs shows that for all of the temperatures 77K-5K, the highest current density was attained with the YBCO film doped with 2 vol. percent BZO + 3 vol. percent Y₂O₃ at a deposition temperature of 825 °C. The associated pinning force curves for this film is shown in Fig. 3(b). Interestingly, in figure 3(a), the double doped 2 vol. % BZO with Y₂O₃ outperforms the single doped 2 vol. % BZO when applied fields exceed 4 tesla. The single doped 2 vol. % film has a matching field of 3 T for 65K, as indicated by the *. The flattening of the current density curve for the double doped film verses the single doped film signifies an increased isotropic behavior, which is confirmed with angular current density measurements in Fig. 3(c)-(d). In the angular current density graphs shown in Fig. 3, Theta = 0˚ corresponds to the field H applied parallel to the c direction, and Theta = 90˚ corresponds to the field H applied parallel to the a-b plane. As the temperature decreases and the applied field increases, the magnitude of the strong pinning due to the dopants at 0˚surpasses the magnitude of the intrinsic pinning at 90˚. Collaborative research with Dr. Judy Wu’s group also showed this benefit of increased isotropic behavior in current density resulting from the utilization of double doping with BZO and Y₂O₃ [10]. Figure 4 shows the variation in critical temperature verses vol. % BZO dopants in YBCO films, also doped with 3 vol. % Y₂O₃, at deposition temperatures of 810 °C and 825 °C. The critical temperatures were degraded at the higher deposition temperature, and for the optimized 2 vol. % double doped BZO film. This corresponds to increased stacking faults seen as deposition temperature increases and is also typical of a tradeoff between increased current densities and lower critical temperatures [11].
Figure 1. Current density as a function of applied field parallel to the c-direction, measured at 77, 65, 20, and 5K for YBCO\textsubscript{100-(x+3)}BZO\textsubscript{x} (x = 2, 4, 6 vol. %) Y\textsubscript{2}O\textsubscript{3} = 3 vol. % at a deposition temperature of 825 °C.

Figure 2. Current density as a function of applied field parallel to the c-direction, measured at 77, 65, 20, and 5K for YBCO\textsubscript{100-(x+3)}BZO\textsubscript{x} (x = 2, 4, 6 vol. %) Y\textsubscript{2}O\textsubscript{3} = 3 vol. % at a deposition temperature of 810 °C.
Figure 3. a) Current density as a function of applied field measured at 65 and 5 K for single doped 2 vol. % BZO and YBCO film and double doped 2 vol. % BZO + 3 vol. % Y₂O₃ YBCO film (STO substrate and 825 °C deposition temperature). Note * signifies matching field for single doped film. b) corresponding pinning force curves for optimized 2 vol. % BZO + 3 vol. % Y₂O₃ doped YBCO film at 65, 50, 20, and 5 K deposited at 825 °C and for YBCO film shown as black curve. Angular dependence of current density measured at (c) 77 K and (d) 65 K at 1T, 3T, 5T, and 9T for 2 vol. % BZO + 3 vol. % Y₂O₃ doped YBCO film deposited at 825 °C.

Figure 4. Critical temperatures (T_c) for 2, 4, and 6 vol. % BZO with 3 vol. % Y₂O₃ doped YBCO films, deposited at 810 °C and 825 °C. Reference T_c for undoped YBCO films shown as black circles.
Microstructure studies involved xrd analysis, along with SEM and TEM. From figure 5(a), the 2 Theta omega scan clearly shows nice epitaxial film growth, and confirms BZO c-axis alignment and the presence of Y₂O₃ for the double doped YBCO films TJ2734, TJ2712 and TJ2768 (2, 4, and 6 vol. % BZO with 3 vol. % Y₂O₃ respectively). Note that the Y₂O₃ peak is absent from the 2 vol. % BZO doped film TJ2856. The rocking curves were measured for the YBCO (005) peak for each of the double doped films. Recall that peak shift indicates macrostrain, and peak broadening indicates non-uniform strain. A FWHM > 0.2 defines a broad peak. Referring to figure 5(b) and Table 2, the non-uniform strain increased as the volume percent BZO increased the double doped films, until some stress relief occurred at 6 vol. % BZO.

![Figure 5](image)

**Figure 5.** (a) XRD 2Theta omega scans for 2, 4, and 6 vol. % BZO with 3 vol. % Y₂O₃ doped YBCO films. (b) XRD rocking curve scans of YBCO (005) peak for 2, 4, and 6 vol. % BZO with 3 vol. % Y₂O₃ doped YBCO films.

| Film # | Composition     | Deposition Temp. °C | FWHM (005) YBCO | β | c-lattice parameter (005) YBCO peak (Å) |
|--------|----------------|---------------------|-----------------|---|----------------------------------------|
| TJ2734 | 2 vol.% BZO + 3% Y₂O₃ | 825 °C             | 0.839           | 0.988 | 11.727                                  |
| TJ2712 | 4 vol.% BZO + 3% Y₂O₃ | 825 °C             | 0.842           | 1.026 | 11.693                                  |
| TJ2768 | 6 vol.% BZO + 3% Y₂O₃ | 825 °C             | 0.489           | 0.665 | 11.732                                  |
From the SEM micrographs in figure 6, one can see how the surface of the film doped with 2 vol. % BZO + 3 vol. % doped YBCO (c,d) contains an increased number of pores and defects in comparison to the YBCO (a,b) film. The effect of the addition of 3 vol. % Y$_2$O$_3$ also has a remarkable impact on the film surface, which can be seen by comparing figure 6 (e,f), the double doped 2 vol. % BZO to figure 6 (g,h), the single doped 2 vol. % BZO film. Interestingly in figure 6(h), within the pores of the film, square shapes are imaged, and are apparently the cross sections of BaZrO$_3$ nanorods (inset), which have a cubic unit cell perovskite structure [12]. The number of pores and defects also increases with increasing deposition temperature, due to the increased adatom mobility (figure 6 e,f). This effect of temperature is also shown with the 4 vol. % BZO double doped film in figure 7(a-d). In comparing figures 6, and 7, the defects and pores and grains also increase with the composition of volume % BZO, with evidence of a-axis film growth associated with the basket weave pattern shown in figure 7(a) [13]. TEM low magnification and high magnification images in figure 8, shows the presence of the second phase dopants, with their density increasing as the volume % BZO of the target utilized increases from 2, 4, and 6 volume % for the double doped BZO films. Due to the proximity of Y and Zr on the periodic table, EDS cannot distinguish between the two with elemental analysis. In figure 8(c) the impact of increased concentration of dopants on the microstructure is evidenced in the degraded film structure and the impact on the BZO nanrod dimensions [10] of the 6 vol. % double doped BZO film on the right compared to the 4 vol. % double doped BZO film on the left.

**Figure 6.** SEM 20kX and 50kX respectively: (a), (b) YBCO (c) (d) 2 vol.% BZO + 3 vol. % Y$_2$O$_3$ doped YBCO on STO substrate at 810 °C deposition temperature; (e), (f) 2 vol.% BZO + 3 vol. % Y$_2$O$_3$ doped YBCO on STO substrate at 825 °C deposition temperature; (g), (h) 2 vol. % BZO doped YBCO on STO substrate at 825 °C deposition temperature.

**Figure 7.** SEM 20kX and 50kX respectively: (a), (b) 4 vol.% BZO + 3 vol. % Y$_2$O$_3$ doped YBCO on STO substrate at 810 °C deposition temperature. (c), (d) 4 vol.% BZO + 3 vol. % Y$_2$O$_3$ doped YBCO on STO substrate at 825 °C deposition temperature. SEM 20kX and 50kX respectively: (a), (b) 6 vol.% BZO + 3 vol.% Y$_2$O$_3$ doped YBCO on STO substrate at 810 °C deposition temperature; (c), (d) 6 vol. % BZO + 3 vol. % Y$_2$O$_3$ doped YBCO on STO substrate at 825 °C deposition temperature.
Figure 8. TEM intermediate and high resolution images respectively: (a) 2 vol. % BZO + 3 vol. % Y₂O₃ doped YBCO on STO substrate at 825 °C deposition temperature. (b) 4 vol. % BZO + 3 vol. % Y₂O₃ doped YBCO on STO substrate at 825 °C deposition temperature. Courtesy of H. Wang’s research group Texas A & M University & Purdue University (c) 4 vol. % BZO + 3 vol. % Y₂O₃ doped YBCO and 6 vol. % BZO + 3 vol. % Y₂O₃ doped YBCO on STO substrate at 825 °C deposition temperature. Courtesy of Kansas University.

4. Conclusion
This research compares the effect of the addition of two insulating, nonreactive phases of barium zirconium oxide (BZO) and yttrium oxide Y₂O₃, both as a single addition of BZO and as a double addition in conjunction with Y₂O₃. Processing parameters vary the target composition volume percent of BZO from 2-6 vol. %, while maintaining 3 vol. % Y₂O₃, and the remaining vol. % YBCO. Pulsed laser deposition produced thin films on LaAlO₃ (LAO) and SrTiO₃ (STO) substrates at various deposition temperatures. XRD confirmed epitaxial, c-axis aligned YBCO films, the presence of the BZO and Y₂O₃ dopant phases, and the resulting stress present in the films. Films produced from the 2 vol. % BZO + 3 vol. % Y₂O₃ doped YBCO target at a deposition temperature of 825 °C attained the highest current density. The addition of second phase Y₂O₃ impacted the film microstructure, resulting in more isotropic behavior when compared to the YBCO films doped with only BZO. This was evidenced in the angular current density measurements, and confirmed by XRD, SEM, and TEM analysis. The 2 vol. % BZO double doped with Y₂O₃ YBCO films achieved higher current density than YBCO films doped only with 2 vol. % BZO at fields greater than 5T at 65K and 4T at 5K, providing insight on tailoring the microstructure to enhance current density at higher fields.
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