

# Reduced $J_c$ anisotropy and enhanced in-field performance of thick BaHfO<sub>3</sub>-doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> films on ABAD-YSZ templates

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**Abstract**—Pure and 6 mol% BaHfO<sub>3</sub> (BHO) doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (YBCO) films were prepared on CeO<sub>2</sub>-buffered ABAD-YSZ templates by pulsed laser deposition. The self-field  $J_c$  at 77 K reaches 1.1 MA/cm<sup>2</sup> in the doped sample compared to 2.5 MA/cm<sup>2</sup> in pure YBCO, at a film thickness of around 1  $\mu$ m. Above a magnetic field of 2.2 T along  $B//c$ ,  $J_c$  of the BHO-doped sample exceeds the  $J_c$  of the undoped film. The maximum pinning force density ( $F_{p,max}$ ) reaches a value of around 3 GN/cm<sup>2</sup> for both samples, but  $B(F_{p,max})$  increases from 1.4 T (pure) to a value of 2.9 T (BHO:YBCO). The  $J_c$  anisotropy curves of the doped sample show a large and broad peak at  $B//c$  and a strongly reduced anisotropy at all temperatures and fields compared to the pure sample. A complex defect structure with YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub> intergrowths, Y<sub>2</sub>O<sub>3</sub> precipitates and BHO nanocolumns with a fan-shaped structure is observed by TEM investigations, which can explain the measured  $J_c(B,\theta)$  behavior.

**Index Terms**—BaHfO<sub>3</sub>, coated conductors, nanocolumns, pinning, YBCO

## I. INTRODUCTION

THE DEVELOPMENT of coated conductors with high current carrying capability for diverse applications is still a hot topic. Especially for the generation of high magnetic fields with superconducting coils it is essential to increase the critical current density in a wide angular range or to reduce the anisotropy. This can be realized by the incorporation of  $c$ -axis correlated secondary phases into the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (YBCO) matrix such as BaHfO<sub>3</sub> (BHO). For our study, we use technical ABAD-YSZ templates which can be produced in long length [1] and focus on films with a thickness relevant for applications (>500 nm).

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It was already shown that the incorporation of BHO can enhance the pinning force density and the irreversibility field in thick YBCO film prepared on technical Ni-9at%W (Ni9W) tape, where the highest values were achieved in the highest tested concentration of 6 mol% BHO [2]. We now transfer this knowledge to ABAD-YSZ templates.

The goal of this paper is a qualitative comparison of the  $J_c(B,T,\theta)$  behavior in pure and 6 mol% BHO-doped YBCO films on ABAD-YSZ templates.

## II. EXPERIMENTALS

### A. Sample preparation

We used a 4 mm  $\times$  10 mm CeO<sub>2</sub>-buffered ABAD-YSZ template, where the Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ) was prepared by alternating beam assisted deposition (ABAD) on a stainless steel metal tape [1]. The sample was heated to 810 °C in a UHV chamber under an O<sub>2</sub> pressure of 0.4 mbar. Afterwards, the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (YBCO) films were deposited by pulsed laser deposition (PLD) using a KrF excimer laser (COHERENT LPXpro 305,  $\lambda = 248$  nm) at an energy density of 1.6 J/cm<sup>2</sup> at the target surface. We used a stoichiometric YBCO target and a target doped with 6 mol% (2.6 vol%) BaHfO<sub>3</sub> (BHO). Targets were mixed from single component powder in the desired stoichiometry, pressed and sintered. Even though we used the same laser conditions for the deposition of pure and BHO-doped films, we observed a different effective growth rate, leading to different film thicknesses (Table I). After oxygenation at 770 °C under 400 mbar O<sub>2</sub> partial pressure for 1 h, the sample was covered at room temperature with around 50 nm silver in another PLD system.

### B. Structural characterization

$\theta$ - $2\theta$  scans were performed with a Bruker D8 Advance Diffractometer (Co anode), and the  $c$ -axis lattice parameters were calculated with the Nelson-Riley method [3]. Cross sections were prepared by focused ion-beam technique (FIB, FEI Helios Nanolab 600i), to determine the film thickness.

Transmission electron microscopy (TEM), bright field transmission electron microscopy (BF TEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were performed on an FEI Titan electron microscope, equipped with an aberration corrector for the probe-forming lens as well as a high-brightness gun, operated at 300 kV and on an FEI Tecnai Osiris electron microscope

operated at 200 kV. TEM cross sectional specimens were prepared via FEI Helios Nanolab 650 FIB. The samples were plasma cleaned before the TEM measurements.

### C. Electrical characterization

The transition temperature ( $T_c$ ) was determined by an inductive method where the shielding of a magnetic field is monitored in dependence of temperature. The given inductively measured  $T_c$  value is comparable to the resistively determined  $T_{c,10}$ , where the 10% criterion of the extrapolated normal state resistance crosses the  $R(T)$  curve. Maps of the critical current density ( $J_c$ ) distribution in the sample were obtained by inversion of the trapped field profile measured by a scanning Hall probe device in liquid  $N_2$  [4]. The listed values correspond to the self-field critical current density  $J_{c,sf}$  at 77 K. The irreversibility field ( $B_{irr}$ ) was determined by fitting  $F_p(B) = J_c \times B$  with the empirical Dew-Hughes function [5]

$$F_p(B) \propto \left( \frac{B}{B_{irr}} \right)^p \left( 1 - \frac{B}{B_{irr}} \right)^q \quad (1)$$

with parameters  $p$  and  $q$ , depending on pinning mechanism and microstructure. To reduce arbitrariness of the fit, the upper limit of  $q$  was set to 2.

The  $J_c$  anisotropy was obtained from magnetization loops measured using a vector vibrating sample magnetometer (VSM). The VSM is equipped with a split coil magnet that can apply fields up to 5 T, and the sample holder can be rotated with a precision of about  $1^\circ$ . The evaluation of  $J_c$  from the width of the hysteresis curve is valid only if the sample is at full field penetration. This leads us to the limitation of the method in evaluating  $J_c$  at  $B \parallel ab$  as the penetrating field diverges.

## III. RESULTS AND DISCUSSION

### A. Basic structural and electrical properties

$\theta$ - $2\theta$  scans (Fig. 1) confirm a pure  $c$ -axis oriented growth of YBCO on the ABAD-YSZ template. The incorporation of BHO into the YBCO matrix leads to an elongated YBCO  $c$ -axis lattice parameter (Table I), which is in agreement with former studies on BHO [2] and  $BaZrO_3/BaSnO_3$  doped films [6]. This is due to the biaxially aligned growth of BHO columns, which results in tensile strain of the  $c$ -axis to adapt the lattice parameters. The lattice parameter of the pseudocubic  $BaHfO_3$  itself was determined from its  $2\theta$  position to be around  $4.15 \text{ \AA}$ , which is close to the bulk value. Aside from the  $c$ -axis peaks, we observe a small  $Y_2O_3$  (004) peak in the pure sample, which is not visible in the BHO doped sample. Most probably  $Y_2O_3$  solutes in BHO, as already discussed in [2].

The  $T_c$  of the BHO-doped sample is around 2 K lower than of the pure YBCO sample (Table I), which was also reported for similar films on Ni9W-tape [2]. The transition widths are in both cases below 1 K, indicating good sample homogeneity.

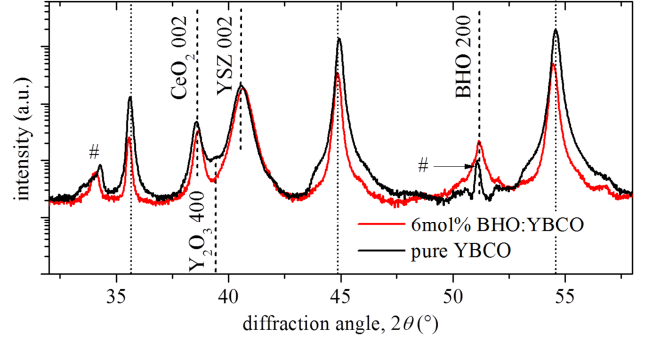


Fig. 1.  $\theta$ - $2\theta$ -scans of the pure YBCO and the BHO:YBCO sample. Peaks of the metallic substrate are labeled with #, dotted lines indicate the position of the YBCO (00 $l$ ) peaks. The relatively broad BHO (200) peak is overlapped by a sharp substrate peak.

TABLE I  
BASIC SAMPLE PROPERTIES

Property (Unit)	Pure YBCO	6 mol% BHO:YBCO
Thickness (nm)	1200	700
$T_c$ (K)	90.2	88.2
$c$ -axis ( $\text{\AA}$ )	11.71	11.76

Using the  $J_c$  maps (Fig. 2), we can determine a typical  $J_{c,sf}$  value of  $2.5 \text{ MA/cm}^2$  for the pure YBCO film and a value of  $1.1 \text{ MA/cm}^2$  for the BHO doped sample (Table II), i.e.  $J_{c,sf}$  is strongly influenced by the doping. In contrast, in BHO-doped YBCO on NiW tape,  $J_{c,sf}$  is independent of the BHO content [2], due to the more dominant grain boundary limitation at low fields.

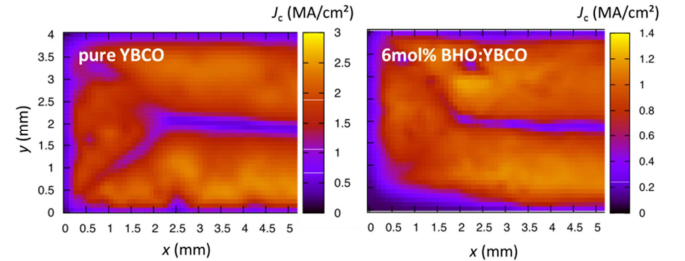


Fig. 2.  $J_c$  maps of one side of the pure and the BHO:YBCO sample with a spatial resolution of  $100 \mu\text{m}$ , obtained from the inversion of the trapped field profiles. The values correspond to the self-field  $J_c$  at 77 K. The low  $J_c$  parts in the middle and the diagonals of the sample are an artifact of the inversion algorithm.

### B. Field dependence of $J_c$ at 77 K

Whereas the undoped sample shows higher  $J_c$  values at low magnetic fields, the BHO-doped sample outperforms the pure YBCO sample above a crossing point at around 2.2 T (Fig. 3). The  $J_c(B)$  curves can be fitted by the relation  $J_c(B) \sim B^\alpha$  in the field range between 0.04 T and 0.8 T, where the power law exponent  $\alpha$  is 0.57 in the pure and 0.32 in the BHO-doped sample. These values agree quite well with earlier measurements on undoped ( $\alpha \sim 0.5$ - $0.6$  [7], [8]) and doped samples ( $\alpha \sim 0.33$  [9]). The crossing point of both  $J_c$  curves generally depends on the  $J_{c,sf}$  value and the slope  $\alpha$  of the curves. Especially  $J_{c,sf}$  is also depending on the film thickness. In 700 nm thick pure YBCO samples an even higher  $J_{c,sf}$  of around  $2.7 \text{ MA/cm}^2$  is expected at 77 K [10], meaning the crossing point would shift to slightly higher fields. But as the pinning

mechanism is not expected to change in this thickness range, it is reasonable to compare these samples qualitatively.

TABLE II  
ELECTRICAL PROPERTIES AT 77 K

Property (Unit)	Pure YBCO	6 mol % BHO:YBCO
$J_{c,sf}$ (MA/cm <sup>2</sup> )	2.5±0.3	1.1±0.2
$\alpha$ -value	0.57	0.32
$F_{P,max}$ (GN/m <sup>3</sup> )	3.2	3.0
$B(F_{P,max})$ (T)	1.4	2.9
$p$	0.55	0.85
$q$	2.0	1.5
$B_{irr}$ (T)	6.6	8.0

The maximal value of the pinning force density is quite similar for both samples ( $\sim 3.1$  GN/m<sup>3</sup>, Table II), but the field  $B_{max} = B(F_{P,max})$  at which the maximal pinning force is achieved is much larger in the BHO-doped sample ( $B_{max} = 2.9$  T) than in the pure one ( $B_{max} = 1.4$  T). Furthermore, the  $F_P$  peak of the BHO sample is much broader, pointing to effective pinning centers in a wider field range.

The best agreement of fitting the  $F_P(B)$ -data by relation (1) was found when  $q$  was set to 2 for the undoped sample and 1.5 for the doped sample (see fitting in Fig. 3 (c)). The  $p$ -value of the doped sample is larger than in the undoped one. This correlates to a smaller  $\alpha$ -value in the low  $B$ -region, where the first term in relation (1) dominates and  $p = 1 - \alpha$ . Additionally,  $B_{irr}$  is increased to 8 T by doping.

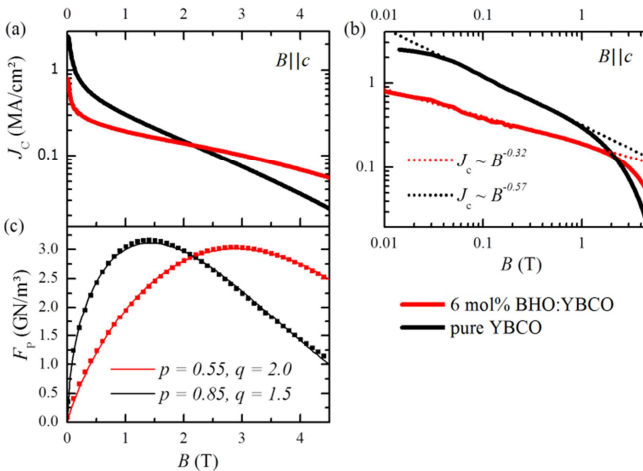


Fig. 3. Field dependence of  $J_c$  at 77 K in (a) single logarithmic and (b) double logarithmic scale and (c) of pinning force density  $F_P$  of the pure and the BHO:YBCO sample. In (c) the fitting according to relation (1) is shown using the parameters in table II and only every tenth data point is plotted.

### C. Angular dependence of $J_c$

Anisotropy measurements were carried out at 77 K and 40 K in the field range from 0.5 T to 4 T. For a better visualization, the  $J_c(\theta)$  curves at different  $B$  were normalized to their values at  $\theta = 90^\circ$  ( $B||c$ ) (Fig. 4).

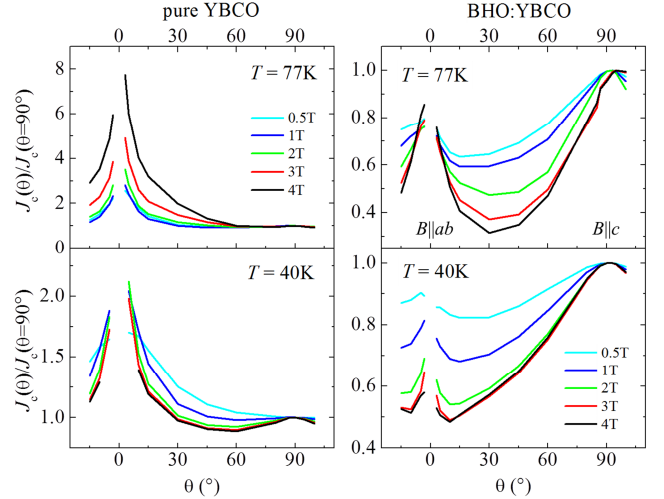


Fig. 4. Angular dependence of  $J_c$  normalized to the value at  $\theta = 90^\circ$  ( $B||c$ ) for two different temperatures and applied fields of 0.5 T to 4 T. Note that the scaling is different.

The pure sample exhibits a large peak at  $\theta = 0^\circ$  ( $B||ab$ ) and a smaller peak at  $\theta = 90^\circ$  ( $B||c$ ) which becomes more visible at lower temperature in high magnetic fields. The anisotropy value  $A = J_c(\theta)_{max} / J_c(\theta)_{min}$  reaches  $\sim 8$  at 77 K and  $\sim 2.5$  at 40 K for a magnetic field of 4 T. In contrast, the anisotropy value in the doped sample is lower ( $A \sim 2$ ) and nearly independent of temperature. In general, we observe an increased anisotropy with increasing field in both samples. In the doped sample, we also find an  $ab$ -peak, but additionally a broad and more dominant  $c$ -axis peak, pointing to very effective pinning centers parallel to the  $c$ -axis. Particularly at 77 K the pinning in  $c$ -direction is as strong as in  $ab$ -direction and almost independent of the magnetic field, but at 40 K it becomes much stronger with increasing field. Already at  $B = 4$  T and  $T = 40$  K,  $J_c$  of the doped sample is higher compared to the undoped sample at all field angles (Fig. 5).

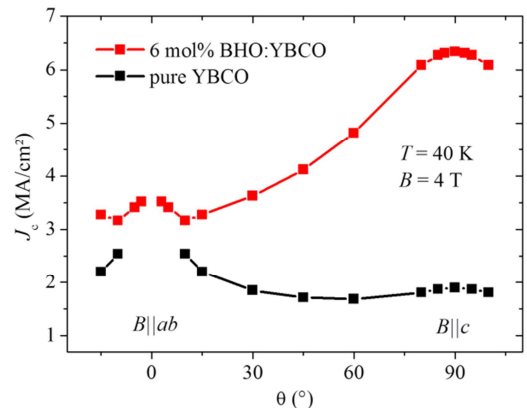


Fig. 5.  $J_c(\theta)$ -curve for the pure and the BHO:YBCO sample at a magnetic field of 4 T and a temperature of 40 K.

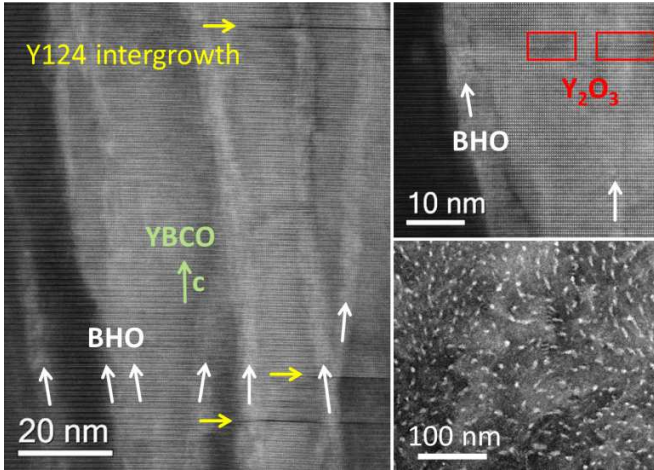


Fig. 6. HAADF STEM Z-contrast image showing nanoscale  $\text{Y}_2\text{O}_3$  precipitates,  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y124) intergrowth and tilted BHO nanocolumns with a typical diameter of 3 nm to 5 nm.

#### D. Microstructure

TEM images of the undoped sample show a dense film with a weak light-dark contrast parallel to YBCO  $c$ -axis direction over the whole film thickness. We attribute this to slightly misoriented YBCO columns (mainly rotation around  $c$ -axis), which are caused by the ABAD-YSZ crystallites through the  $\text{CeO}_2$  cap layer [11]. These small angle [001]-tilt boundaries, are assumed to be mainly responsible for the small peak in the angular dependence at  $\theta = 90^\circ$  ( $B||c$ ) in the undoped film (Fig. 4).

TEM images of the BHO-doped sample show a flat and dense film with a complex microstructure, featuring a few nanoscaled  $\text{Y}_2\text{O}_3$  precipitates with a size of around 10 nm,  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y124) intergrowths and BHO nanocolumns with a typical diameter of 3 nm to 5 nm (Fig. 6). The nucleation of the BHO columns starts right on the  $\text{CeO}_2$  buffer layer, and some columns can be tracked almost the whole thickness of the film. We find two kinds of areas. In some parts, the columns grow straighter and parallel to the YBCO  $c$ -axis and so to the film normal direction. In other regions, we observe a fan-shaped growth of BHO (Fig. 7). High-resolution images of fan-shaped areas (Fig. 6) show that these columns are tilted and winding, still being biaxial oriented to YBCO. The tilt angle of the BHO columns towards the YBCO  $c$ -axis is about  $10^\circ$  for long pieces (length  $\sim 400$  nm) and up to  $20^\circ$  for shorter segments (length  $\sim 100$  nm). This could explain why the  $c$ -axis peak in the  $J_c$  anisotropy curve is broad and the addition of BHO leads to an increased  $J_c$  in a wide angular range.

A similar structural formation of tilted columns of dopant material has been observed in YBCO films with YSZ and  $\text{BaZrO}_3$  doping [6], [9], and in BHO doped  $\text{SmBa}_2\text{Cu}_3\text{O}_y$  films [12 - 13] prepared by PLD on single crystalline substrates. In all these cases an enhanced performance of  $J_c(B)$  at  $B||c$  was measured and in [6], [9] a broad and dominant peak was observed in the angular measurement at  $B||c$ .

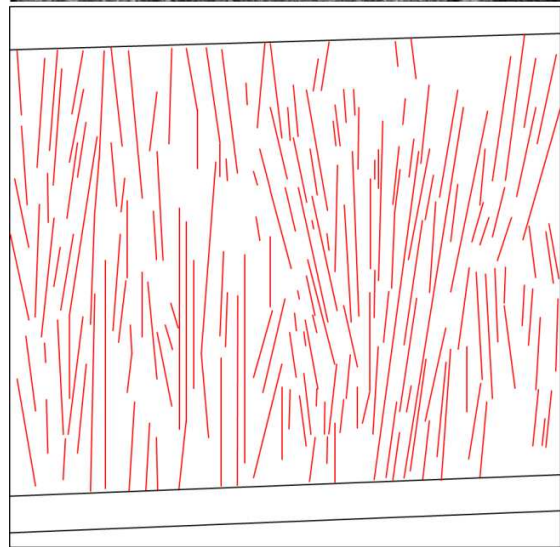
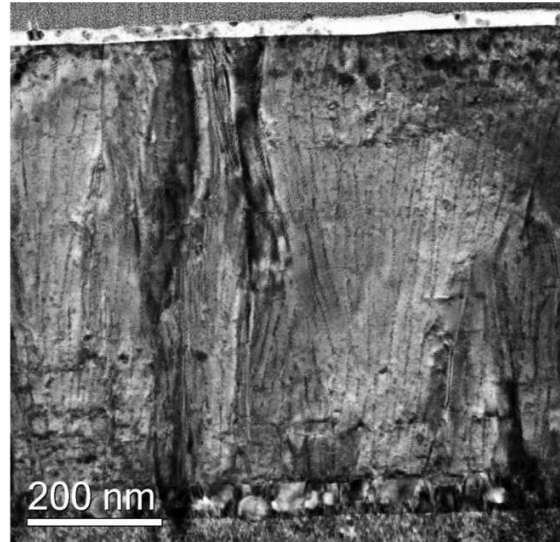


Fig. 7. Upper part: BF TEM image of the cross-section of the BHO doped sample. Lower part: Drawing of length and orientation of clearly identifiable BHO nanocolumns showing a fan-shaped structure.

#### IV. CONCLUSION

6 mol% BHO doping was successfully implemented into YBCO based coated conductors prepared on ABAD-YSZ templates. We find a fan-shaped growth of BHO nanocolumns which lead to a broad peak in the anisotropy curves around  $B||c$  and a reduction of the  $J_c$  anisotropy. The effect of these pinning centers is more dominant at higher fields and lower temperature. In comparison to the undoped reference sample the BHO sample shows a better  $J_c$  performance at all field angles at 40 K and 4 T.

#### ACKNOWLEDGMENT

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