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GROWTH AND OPTIMIZATION OF HIGH-PERFORMANCE THICK REBCO
FILMS FOR APPLICATION OVER A WIDE RANGE OF TEMPERATURE (77 - 4.2)
K AND MAGNETIC FIELDS (0 – 15) T

A Dissertation

Presented to

the Faculty of the Department of Mechanical Engineering

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In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Materials Science and Engineering

by

Rudra Pratap

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GROWTH AND OPTIMIZATION OF HIGH-PERFORMANCE THICK
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Abstract

Rare Earth Barium Copper Oxide (REBCO) coated conductors are the only superconductors with a potential for applications over broad range of temperature (77 K – 4.2 K) and wide range of fields (0 – 20 T and above). However, its high cost compared with other available superconductors is a major bottleneck in realizing its desired potential and wide range of applicability.

Reducing cost of REBCO in terms of (\$/kA-m) can be accomplished by further improving the engineering current density (J_e) of these superconductors and reducing the manufacturing cost. J_e can be improved in two different ways - by incorporating pinning centers and by increasing thickness ($> 2 \mu\text{m}$) without deterioration of critical current density (J_c). Increasing pinning centers has a certain limit, after which the critical current degrades. Increasing thickness of REBCO without any deterioration in J_c is a direct way forward to achieving high J_e . However, increasing thickness ($> 2 \mu\text{m}$) of REBCO has always led to decrease in J_c , independent of the deposition method used. The major obstacle here is poor process control, a high J_c could not be maintained along the thickness, while growing thicker films ($> 2 \mu\text{m}$).

In the present work, thick (3.5 -5 μm) undoped and doped REBCO films were grown using an advanced MOCVD (A-MOCVD) reactor. Several different studies have been conducted to optimize compositions in order to achieve high performance for high temperature, low field application with good isotropic behavior and for low temperature, medium - high field applications. Record high I_c of 1440 A/cm at 65 K, 1.5 T ($B \parallel c\text{-axis}$) and a minimum I_c of 1740 A/cm at 65 K, 0.25 T have been attained in 4.7 μm 5 mol% Hf-doped REBCO films. Also, engineering current density (J_e) over 5 kA/mm² ($\sim 5X \text{ Nb}_3\text{Sn}$)

has been achieved in a 4.8 μm thick, 15 mol% Zr-doped REBCO at 4.2 K, 14 T ($B \parallel c$ -axis).

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List of Abbreviations

REBCO	REBa ₂ Cu ₃ O _{7-δ} (RE=Gd, Y)
(Gd, Y)BCO	(Gd, Y)Ba ₂ Cu ₃ O _{7-δ}
HTS	High Temperature Superconductors
LTS	Low Temperature Superconductors
1G-HTS	First Generation High Temperature Superconductors
2G-HTS	Second Generation High Temperature Superconductors
CCs	Coated Conductors
I _c	Critical Current
J _c	Critical Current Density
J _e	Engineering Critical Current Density
T _c	Critical Temperature
ΔT _c	Superconducting Transition Width
H _c	Critical Magnetic Field
H _{c,1}	Lower Critical Magnetic Field
H _{c,2}	Upper Critical Magnetic Field
F _p	Pinning Force
F _L	Lorentz Force
λ	Penetration Depth
ξ	Coherent Length
Φ ₀	Quantum Flux
Ψ	Superconducting Order Parameter
PIT	Powder in Tube
Bi-2223	Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀
APCs	Artificial Pinning Centers
BZO	BaZrO ₃
IBAD	Ion Beam Assisted Deposition
RABiTS	Rolling Assisted Biaxially Textured Substrate

ISD	Inclined Substrate Deposition
GADDs	General Area Detector Diffraction System
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
ICP-MS	Inductive Coupled Plasma – Mass Spectrometry
MOCVD	Metal Organic Chemical Vapor Deposition
MOD	Metal Organic Deposition
PLD	Pulsed Laser Deposition
THF	Tetrahydrofuran
SCCM	Standard Cubic Centimeters per Minute

Chapter 1. Introduction

This chapter gives a brief overview of the basics of superconductivity, different types of superconductors and their properties, flux pinning mechanisms in superconductors, REBCO fabrication processes and different ways of improving critical current of REBCO. This is used as background information to illustrate the diverse aspects of the research work presented in this study.

1.1. Introduction to Superconductivity.

Three years after the first liquefaction of helium, superconductivity was first discovered by H. Kamerlingh Onnes in Leiden in 1911 [1]. Onnes observed complete disappearance of the electrical resistance of mercury (Hg) at 4.2 K, which jumped from an immeasurably small value (less than 10^{-6} ohm) to the 0.1 ohm, within the span of 0.01 K [2], indicating a sudden drop in resistance below a critical temperature T_c . To confirm the absence of resistance in superconductors, Onnes induced current in a superconducting loop and observed no decay in the current.

Superconductivity is a property of certain materials that show zero resistance when cooled below a certain critical temperature. Critical temperature (T_c) is the temperature below which a superconductor loses its electric resistance, and the width of the transition from the normal state ($T > T_c$) to the superconductor state ($T < T_c$) is defined as the superconducting transition width (ΔT_c). The decrease in resistivity of conductors with temperature is shown in Figure 1-1 [3]. While metals have some resistance even at absolute zero temperature (0 K), superconductors exhibit zero resistance below T_c .

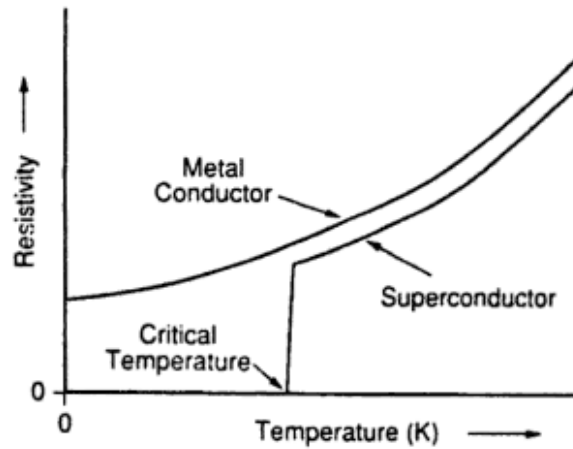


Figure 1-1. Resistivity-temperature diagram for metal and superconductor.

1.1.1 Basic phenomena of superconductors

Perfect diamagnetism was revealed as a fundamental phenomenon of superconductivity by Meissner and Ochsenfeld in 1933 [4]. They observed that a weak applied magnetic field gets expelled from all of the interior of a superconductor except for a thin layer at the surface. The magnetic field is not only excluded from entering a superconductor, as might be in the case of the perfect conductor, but also can be expelled from an originally magnetized sample when it is cooled below T_c . The occurrence of the Meissner effect suggests that superconductivity could be destroyed by a critical magnetic field H_c , which is thermodynamically related to the free energy difference between the normal and superconducting state.

In 1935, Fritz and Heinz London proposed that although the magnetic field is expelled from superconductors, it penetrates to a small thickness inside the superconductor's surface, which is known as the penetration depth [5]. In 1955, Ginzburg provided insight into the macroscopic theory of superconductivity [6]. BCS theory (named after John Bardeen, Leon Cooper, and Robert Schrieffer) emerged in 1957, providing a

microscopic theory of superconductivity [7]. In 1957, Abrikosov proposed a new type of superconductor (Type-II superconductors), in which the magnetic flux penetrates as a regular array of quantum vortices when above a certain critical field [8]. This unique kind of flux penetration, often called as the ‘mixed state’, exists only in Type-II superconductors.

1.1.2 Superconducting critical values

Three major critical values that affect superconductivity are critical current density (J_c), critical magnetic field (B_c), and critical temperature (T_c). The maximum current density that a superconductor can carry at a given temperature and applied magnetic field is defined as a critical current density (J_c). As mentioned above, critical temperature (T_c) is defined as the temperature above which material loses its superconductivity. Similarly, the critical magnetic field (B_c) denotes a certain limit of the applied magnetic field beyond which flux lines start penetrating the materials and material’s superconductivity is destroyed. All three critical values J_c , B_c and T_c are interconnected and changing one critical value affects the other two. Plotting all three critical values in the same coordinate system defines a critical surface as shown in Figure 1-2. T_c , J_c and B_c for different superconductors like Nb_3Sn , $YBa_2Cu_3O_7$, MgB_2 and Fe-based superconductors are depicted in Figure 1-2 [9]. Materials are superconducting when their J_c , T_c and B_c are at or below each of the critical values.

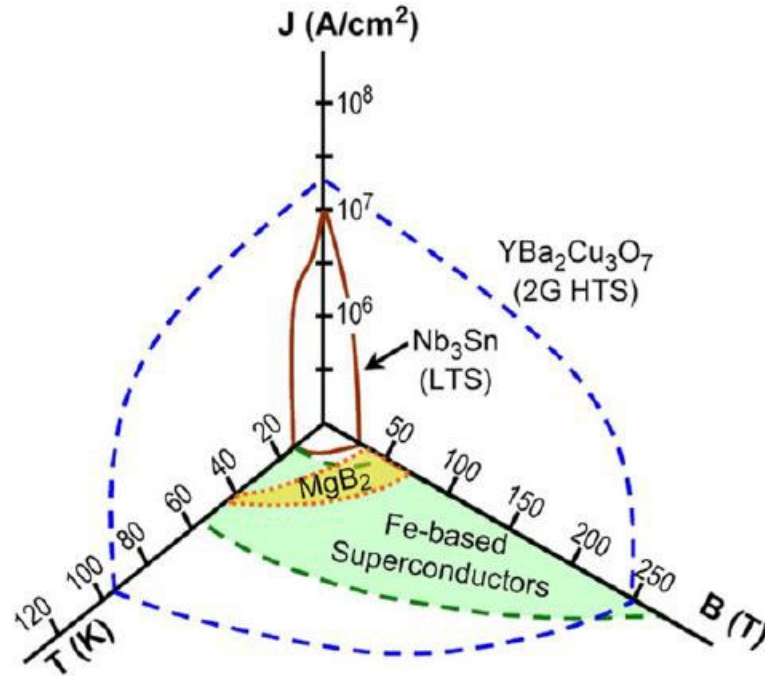


Figure 1-2. T_c , J_c and B_c of Nb_3Sn , $YBa_2Cu_3O_7$, MgB_2 and Fe-based superconductors.

1.1.3 Discovery of superconductors

Discovery of the first superconductor (Hg) in 1911 by H.K. Onnes sparked a worldwide interest to find superconductors with higher T_c , which led to a discovery of several superconductors in the last century including metals, alloys, and compounds. The timeline of the discovery of superconductors over a century is shown in Figure 1-3 [10] where dark green circles depicts BCS superconductors (conductors that obey BCS theory), blue diamonds depicts cuprates, purple inverted triangle indicates Buckminsterfullerene, red triangle shows carbon allotrope and orange-yellow square depicts Iron pnictogen.

Nb has the highest critical temperature of 9 K, among the various metal superconductors. Generally speaking, superconductors with T_c below 23 K are called low-temperature superconductors, and the ones with T_c above 23 K are called high-temperature superconductors [11]. Nb_3Sn and $NbTi$ are the most widely-used low-temperature

superconductors with T_c of 18 K and 9.2 K, respectively [12,13]. In 1980, Ba-La-Cu-O was the first high-temperature superconductor with $T_c \sim 30$ K, discovered by Bednorz and Muller [14]. Soon after, in 1987, a major breakthrough occurred with the discovery of the first high-temperature superconductor, Y-Ba-Cu-O ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$), that has a T_c (~ 93 K) above liquid nitrogen temperature (77 K), by the University of Alabama-Huntsville and University of Houston [15]. This was a big breakthrough since these superconductors can theoretically be used with a 100 times less expensive cryogen (liquid nitrogen) when compared with liquid helium required for application of LTS. Several other cuprate superconductors have been discovered with T_c above that of liquid nitrogen such as those in the Bi-Sr-Ca-Cu-O (BSSCO) system with maximum T_c of 110 K [16], in the Tl-Ca-Ba-Cu-O system [17] with maximum T_c of 120 K and in the Hg-Ba-Ca-Cu-O system with $T_c > 130$ K [18]. Nagamatsu et al. in 2001 discovered superconductivity in magnesium diboride (MgB_2) at 39 K as a new class of non-cuprate HTS [19].

Since the discovery of superconductors, there has been a lot of progress in making these magnificent materials feasible for industrial applications. The most widely used superconductors are NbTi (LTS), Nb_3Sn (LTS), BSSCO (HTS), REBCO (HTS) and MgB_2 (HTS). Due to their different critical magnetic fields and critical temperatures, these superconductors are used for different fields of applications. NbTi is widely used in magnets up to 9 T at 4.2 K: most of the magnets in MRI systems are made of NbTi wires [20,21]. Nb_3Sn can be used for magnets that requires higher fields (useable upto 15-20 T at 4.2 K), however the brittleness of this material makes the winding of Nb_3Sn wire difficult [20,22]. NbTi and Nb_3Sn superconducting wires have been widely used in several particle accelerator projects such as Hadron-Electron Ring Accelerator, Hamburg, Germany;

Fermilab, Chicago and Large Hadron Collider, European Organization for Nuclear Research (CERN), Geneva, Switzerland [23]. MgB_2 is viable for use in low-to-medium magnetic field applications, such as sensitive magnetic field detector [24]. Above 20 T magnetic field, Bi-2212 (BSSCO) and REBCO are the most suitable superconductors for applications [20,25,26].

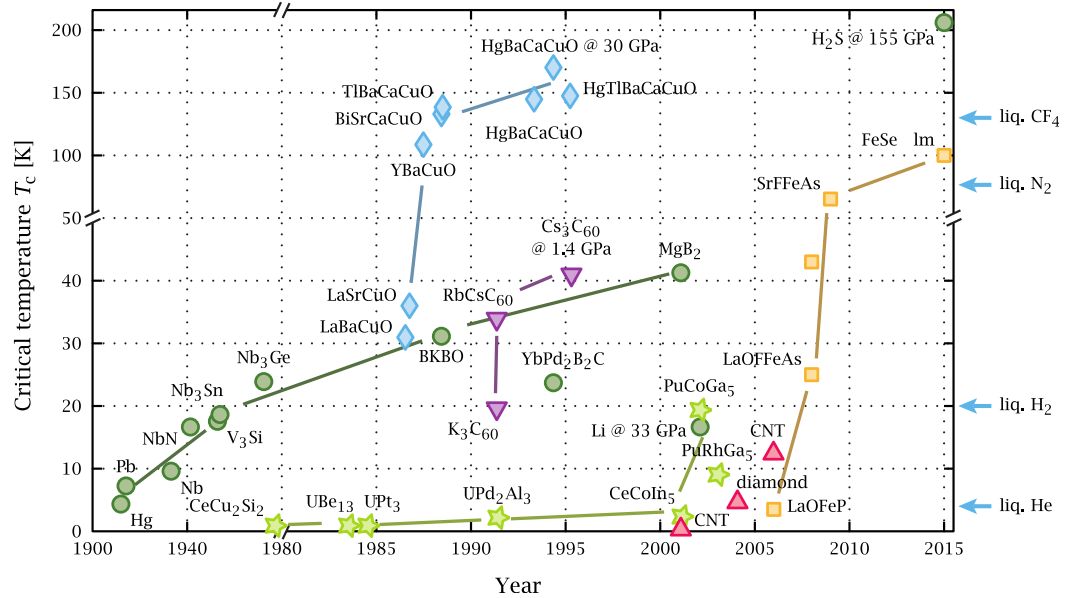


Figure 1-3. Timeline of discovery of different superconductors from 1900 to 2015.

1.1.4. Type-I and Type-II superconductors

All superconductors are broadly classified into two groups, Type-I and Type-II superconductors, based on their transition from normal to the superconducting state. As shown in figure 1-4, type-I superconductor has one critical field (H_c) while type-II superconductors have two critical fields: lower critical field (H_{c1}) and upper critical field (H_{c2}) [27].

Type-I superconductors are usually pure metals like Hg, Nb, etc, which show zero resistance and Meissner effect below the critical field (H_c) and a normal state above H_c .

Since H_c of type-I superconductors is in the small range of few mT, these superconductors lose their superconductivity very easily and abruptly, which makes them not very useful in applications.

Type-II superconductors exhibit Meissner state below the lower critical field (H_{c1}) and normal state above the upper critical field (H_{c2}), as shown in Figure 1-4. In between the lower critical field (H_{c1}) and upper critical field (H_{c2}), exists a mixed state in which magnetic flux lines penetrate through the superconductors in the form of vortices or fluxons, each of which has a constant value of flux quantum: $\Phi_0 = h/(2e) = 2.07 \times 10^{-15} \text{ Wb}$ [8]. The mixed state is still a superconducting state and has zero resistance. Type II superconductors have several potential applications of interest due to the presence of this mixed state, where the upper critical field can be over a hundred Tesla. The temperature dependence of critical fields (H_c , H_{c1} , and H_{c2}) for both type-I and type-II superconductors is given by [28]:

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right], \quad (1-1)$$

where $H_c(0)$ and $H_c(T)$ are critical fields at absolute zero temperature and a specific temperature.

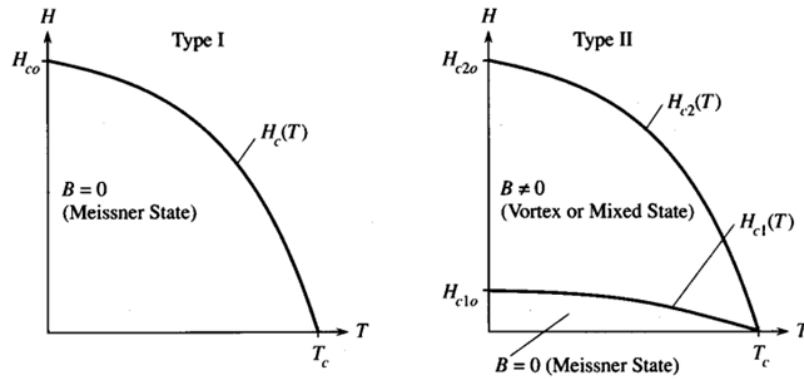


Figure 1-4. Magnetic field and temperature phase diagram of Type-I and Type-II superconductors.

Type-I and Type-II superconductors can also be distinguished using the Ginzburg-Landau dimensionless parameter (κ), which is given by [29,30]:

$$\kappa = \frac{\lambda_L}{\xi}, \quad (1-2)$$

where λ_L is the penetration depth of the magnetic field and ξ is the coherence length between the electrons in a Cooper pair.

Type-I superconductors have $0 < \kappa < \frac{1}{\sqrt{2}}$ while for type-II superconductors, $\kappa > \frac{1}{\sqrt{2}}$.

It is important to also discuss surface free energy between type-I and type-II superconductors, which is given by

$$g_{surface} = \frac{1}{2} \mu_0 H_c^2 (\xi - \lambda_L), \quad (1-3)$$

where $g_{surface}$ is the free energy between the normal and superconducting phases and μ_0 is the magnetic permeability [29-30].

According to equations (1-2) and (1-3), type-I superconductors have positive surface energies while type-II superconductors have negative surface energies.

1.1.5. First generation and second generation high-temperature superconductors

As mentioned above, the most common and widely-used high-temperature superconductors are BSSCO and REBCO, which are named as first generation (1G) HTS and second generation (2G) HTS respectively.

1.1.5.1. 1G HTS - BSCCO

1G HTS, which is bismuth-based Bi-Sr-Ca-Cu-O (BSCCO) is the first high-temperature superconductor that was made as long wires [31]. BSCCO is fabricated using

the powder-in-tube method with the superconductor filaments embedded in a silver matrix. Figure 1-5 shows a schematic of the powder-in-tube process, used for fabrication of Bi-2223 [32]. In this process, fine powders of the starting ingredients are filled into a silver tube which is then drawn into a small-diameter wire. These small diameter filaments are then cut into many small segments which are then further assembled in another silver tube to be drawn into a multifilament wire. This wire is then rolled into a tape and sintered to form 4 mm wide Bi-2223 tape. A second rolling and sintering are finally performed to align the micaceous grains in the plane of the tape. These tapes can carry over 100 Amps at liquid nitrogen temperature and are flexible enough to be used for commercial applications [33]. BSCCO is produced in hundreds of kilometres of tape for various applications like power cables. However, BSCCO depends heavily on the use of silver, which makes it too expensive for most commercial applications [33]. Another issue with BSCCO is its poor critical current in the presence of a magnetic field at liquid nitrogen temperature. In the presence of magnetic field, BSCCO has higher anisotropy and lower irreversibility field in comparison with REBCO (2G HTS), which makes it less favorable to be used in motors or generators [33].

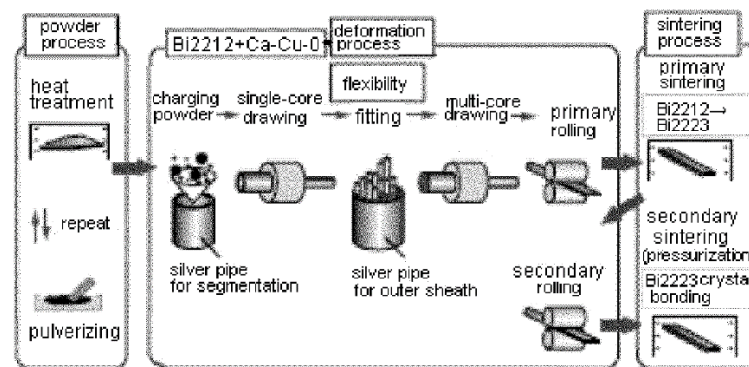


Figure 1-5. Schematic illustration of the powder in tube process for 1G HTS (BSSCO) fabrication.

1.1.5.2. 2G HTS – REBCO

Second generation high-temperature superconductors are REBCO (Rare earth barium copper oxide). REBCO (or (Gd, Y)Ba₂Cu₃O_{7- δ}) has an orthorhombic three-layered perovskite structure as shown in Figure 1-6 [34]. Cu(1) are the copper atoms along the b-axis which form CuO chains, while Cu(2) are the copper atoms as part of in-plane CuO₂ layers forming CuO₂ planes. Superconducting properties of YBCO are determined by charge transfers between the conducting CuO₂ planes and the charge reservoir CuO chains [35]. δ in YBa₂Cu₃O_{7- δ} represents the oxygen deficiency in the structure. Before oxygenation, when $\delta \geq 0.5$, YBCO has a tetragonal structure which is not a superconducting phase, while after oxygenation when $\delta < 0.5$, YBCO changes to an orthorhombic structure which is a superconducting phase. The lattice parameter values for orthorhombic YBCO structure are: $a = 0.382$ nm, $b = 0.389$ nm, and $c = 1.168$ nm while for tetragonal structure ($a = b \neq c$, all angles = 90°) lattice parameter values are: $a = b = 0.386$ nm, and $c = 1.168$ nm. The transition temperature of YBCO is affected by the oxygen content, which is shown in Figure 1-7 [35].

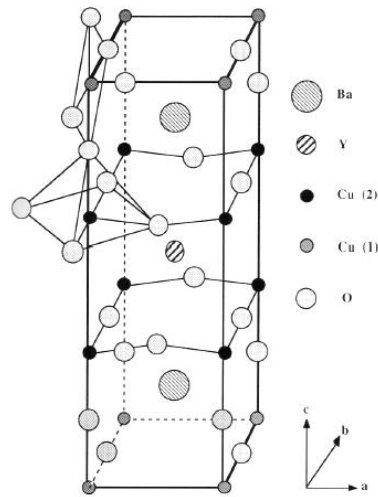


Figure 1-6. Schematic of YBCO unit cell structure.

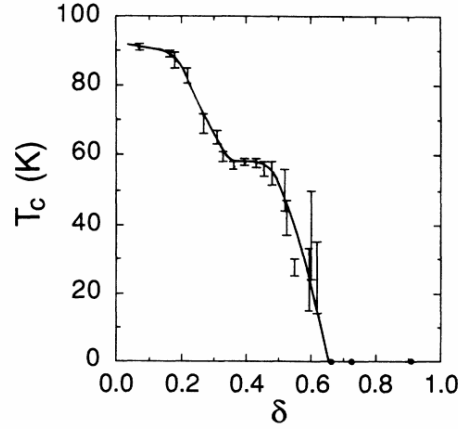


Figure 1-7. Critical temperature (T_c) dependence of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on the oxygen deficiency (δ) content in the unit cell.

1.2. Flux pinning mechanism

1.2.1. Flux vortices

As mentioned above, in type-II superconductors, the magnetic field in a mixed state penetrates through the superconductor in the form of magnetic flux lines called vortices [8]. These vortices are like non-superconducting cores, which are surrounded by circulating superconducting currents [36]. Figure 1-8 shows the cross-section of an isolated vortex with the magnetic field distribution and order parameter amplitude. The superconducting order parameter (Ψ) decreases to zero at the center of the vortex where no Cooper pairs exist.

Cooper pair density rises to a maximum within the coherence length (ξ). The core radius of the vortices is provided by the coherence length (ξ), and the circulating supercurrent extends till the penetration depth (λ), which is around 100-200 nm [36]. A single core vortex carries magnetic field equal to flux quantum, $\Phi_0 = \frac{hc}{2e} = 2.068 \times 10^{-7}$

G.cm². Figure 1-9 shows a real-time image of vortices in 200 nm thick YBCO captured using Scanning SQUID Microscopy after field cooling at 6.93 μ T to 4 K [37]. At sufficiently low temperatures and in the absence of any disorder, these vortices form a regular lattice called as an Abrikosov lattice [36]. Abrikosov lattice of vortices are highly affected by the change of temperature and the amount of disorder present in the structure. Increasing temperature increases thermal fluctuations that transform an Abrikosov lattice into the vortex liquid phase in which vortices can freely slide against each other [36]. At lower temperatures too, this regular array of vortices can be destroyed by the presence of strong disorder in the superconducting materials, which leads to a vortex glass state [36].

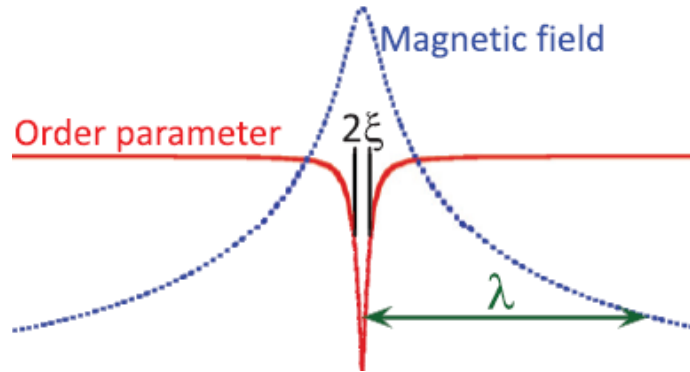


Figure 1-8. Structure of an isolated vortex.

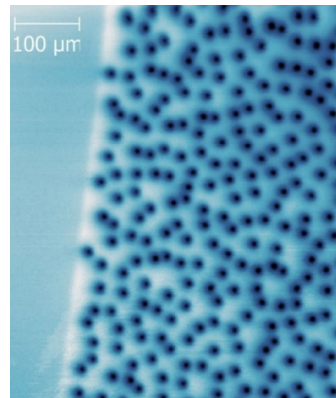


Figure 1-9. Images of vortices in 200 nm thick YBCO film taken by Scanning SQUID Microscopy after field cooling at 6.93 μ T to 4 K.

Applications of superconductors are mainly based on their lossless high critical current capability. The high critical current capability of the superconductor depends on the interaction of the current flowing through the superconductor with the vortex states that arise due to either an external applied magnetic field or the applied current itself. Figure 1-10 shows a schematic diagram of magnetic flux vortices experiencing a Lorentz force due to the current flowing through the superconductor [38]. In the mixed state of type-II superconductors, an external electric current (J) generates a Lorentz force (F_L) on the vortices, which is given by

$$F_L = J \times B. \quad (1-4)$$

Applying an electric current to the type-II superconductor in a mixed state generates a Lorentz force (F_L) leading to the motion of vortices with velocity (v). The motion of vortices generates an electric field (equation 1-5), parallel to electric current and perpendicular to the velocity, leading to dissipation of energy and occurrence of ohmic resistance. Hence, the loss of superconductivity. The electric field (E) is given as

$$E = B \times v. \quad (1-5)$$

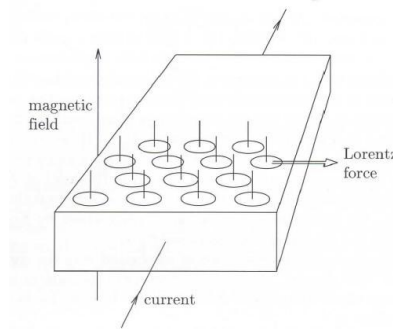


Figure 1-10. Magnetic flux lines (vortices) applied perpendicular to the superconductor, experiencing Lorentz force by the current flowing through the superconductor material.

High critical current density in high-temperature superconductors can only be achieved if these vortices are immobilized using pinning centers, by generating a counteracting pinning force. The pinning force (F_p) for type-II superconductors can be calculated using the Dew-Hughes model [39] as shown below:

$$F_p = J_c \times B, \quad (1-6)$$

when $F_p > F_L$, the flux vortices remains pinned but as F_L increases (either with an increase in current density or applied magnetic field) and becomes equal to $F_{p, \max}$, vortices start moving. This stage can be seen by the appearance of a voltage in the I-V (current-voltage) curve. The corresponding current density (J_c) when $F_L = F_{p, \max}$ is called critical current density (J_c).

1.2.2. Pinning defects in REBCO

The critical current density of REBCO can be enhanced by introducing pinning centers in the superconducting materials that can immobilize vortices and avoid dissipation of energy. Pinning defects in REBCO coated conductors can be broadly classified into two types: intrinsic and extrinsic defects.

Intrinsic pinning in REBCO results from the presence of a weak superconducting layer between strongly superconducting CuO_2 planes. This weak superconducting layer acts as a pinning center in the a-b plane direction, which can be observed as a strong peak in the critical current density when the magnetic field is oriented parallel to a-b direction [40]. It has also been shown that when the magnetic field is oriented at an angle to the a-b plane of REBCO, flux lines can be pinned by its weak superconducting layer in the ab plane as shown schematically in Figure 1-11 [41].

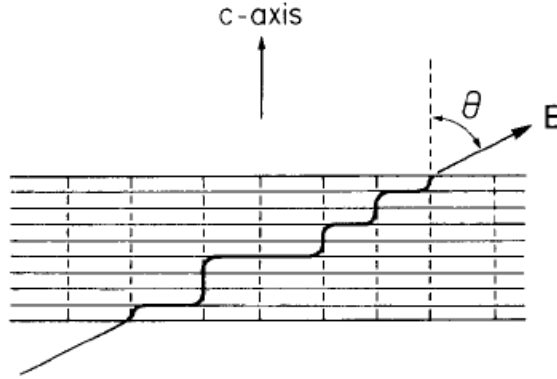


Figure 1-11. Stepwise flux lines piercing through the layered structure of YBCO at an angle θ . Weakly superconducting planes are indicated by horizontal lines, and twin planes are indicated by vertical dashed lines.

Extrinsic pinning defects in REBCO can be broadly classified as correlated and uncorrelated (or random) pinning defects. Correlated pinning occurs from parallel arrays of planar or extended linear defects. Correlated pinning is the strongest when the applied magnetic field is along the growth direction of these defects and decreases as the angle between the applied field and correlated defects increases [33]. Uncorrelated or random pinning is due to randomly localized defects which improve pinning in every orientation of the applied magnetic field. In comparison, when the magnetic field is aligned along the growth direction of the defects, correlated pinning defects offer much stronger pinning than uncorrelated defects, since the pinning force on trapped vortices increases linearly with vortex length, as does the Lorentz force [33].

These crystalline extrinsic defects can also be classified in several other different ways. For example, based on dimensionality of the defects, these can be classified as the following different types of artificial pinning centers (APC) [42][36]:

- (1) Zero-dimensional defects : Any defects whose size is smaller than the coherence length (ξ), like cation disorder [43] or oxygen vacancies [44].

- (2) One dimensional or line defects : columnar defects (nanocolumns using irradiation [45], self assembled nanocolumns (BaZrO_3 , BaHfO_3)[46–50]), screw or edge dislocations [51].
- (3) Two dimensional defects: small angle grain boundaries [52], surface of large precipitates [52], stacking faults, twin boundaries.
- (4) Three-dimensional defects: Nanoparticles or any secondary phase with the size of ξ or larger.

A schematic view of the above described different types of artificial pinning centers classified based on their dimensions is shown in figure 1-12 [42].

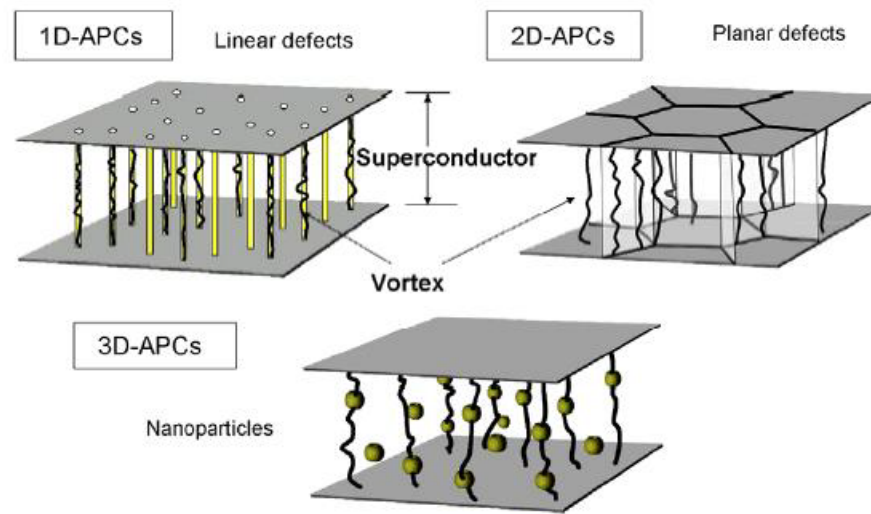


Figure 1-12. Schematic of different types of artificial pinning centers depending on their dimensions.

One and two-dimensional defects are often referred to as correlated defects [36]. Zero-dimensional and three-dimensional defects generally come under random defects. RE_2O_3 precipitates, voids, defect clusters, irradiation collision clusters come under large random defects [36].

For these defects to act as effective pinning centers, their size needs to be in the proximity of 2ξ . If the size of the non-superconducting defect is smaller than 2ξ , it cannot completely pin the flux line, while if its size is much larger, then it would reduce the superconducting volume that will decrease the current carrying capability of the material. Hence, it is very important to properly tailor the pinning landscape in REBCO to obtain high performances at the required temperature and applied magnetic field.

Among all the defects named above, self-assembled nanocolumnar defects and RE_2O_3 precipitates have been the most extensively researched, and have shown great promise in improving the J_c of REBCO in applied magnetic fields.

Self-assembled nanocolumnar defects are classified in the category of one-dimensional correlated defects. These columnar defects shows very strong pinning at high temperatures when the magnetic field is applied along the columnar defects growth direction (usually $B \parallel c$ -axis).

1.3. Fabrication of REBCO (YBCO)

Since the discovery of YBCO in 1987, there has been tremendous progress in the effort to making this superconductor viable for commercial applications. During the early years of its discovery, YBCO was fabricated using powder sintering, which resulted in lower critical current density (J_c) due to weak links at grain boundaries. The existence of a large number of semi-coherent and incoherent grain boundaries can adversely effect J_c [53]. Grain alignment by using melt-texture growth process results in higher J_c values [54]. However, these improvements yield only a limited amount of improvement in transport properties.

Further progress has been achieved in depositing thin films of these materials on flexible substrates.

1.3.1. REBCO thin film growth

1.3.1.1. Substrate

Choosing the right substrate plays a vital role in obtaining high performance in REBCO thin films. Choice of substrate depends on the specific desired application of the deposited thin REBCO film like for microwave applications, substrate with low microwave losses should be preferred. The basic requirement for the selection of substrate can be described as follows [55]:

- The thermal expansion coefficient of substrate should be similar to that of REBCO.
- The substrate must be stable and robust.
- The substrate must be chemically inert to REBCO during the deposition process.
- The substrate should have good lattice match with REBCO films.

Several methods like rolling-assisted biaxially textured substrate (RABITS), ion beam assisted deposition (IBAD) and inclined substrate deposition (ISD) have been developed to make biaxially-textured buffer layers suitable for high performance REBCO films.

1.3.1.2. Deposition method for REBCO thin film growth

There are several different deposition methods that can be used to grow thin REBCO films. These can be broadly classified into physical and chemical vapor deposition techniques as shown below:

1. Physical vapor deposition techniques: In this type of deposition, vaporized form of the materials created by physical means are condensed and deposited onto a surface. These methods generally have a lower deposition rate and require expensive vacuum systems. Examples are Pulsed Laser Deposition (PLD), Sputtering and Reactive Co-evaporation (RCE).
2. Chemical vapor deposition techniques: Methods comprise of Chemical Vapor Deposition (CVD), Metal Organic Chemical Vapor Deposition (MOCVD), Metal-Organic deposition (MOD), liquid phase epitaxy, and Chemical Solution Deposition (CSD). These methods have a relatively higher deposition rate and do not require very high vacuum for the process.

All the process of deposition can be divided into three steps as shown in figure 1-13. The particle source includes a mixture of organic molecules (for MOCVD), chemical solution (for CSD), stoichiometric HTS compound (for PLD). Next step is particle transport from the target source to the substrate. The final step is nucleation/phase formation which represents actual formation of the thin film on the substrate. This depends on different process parameters (like substrate temperature, process pressure etc).

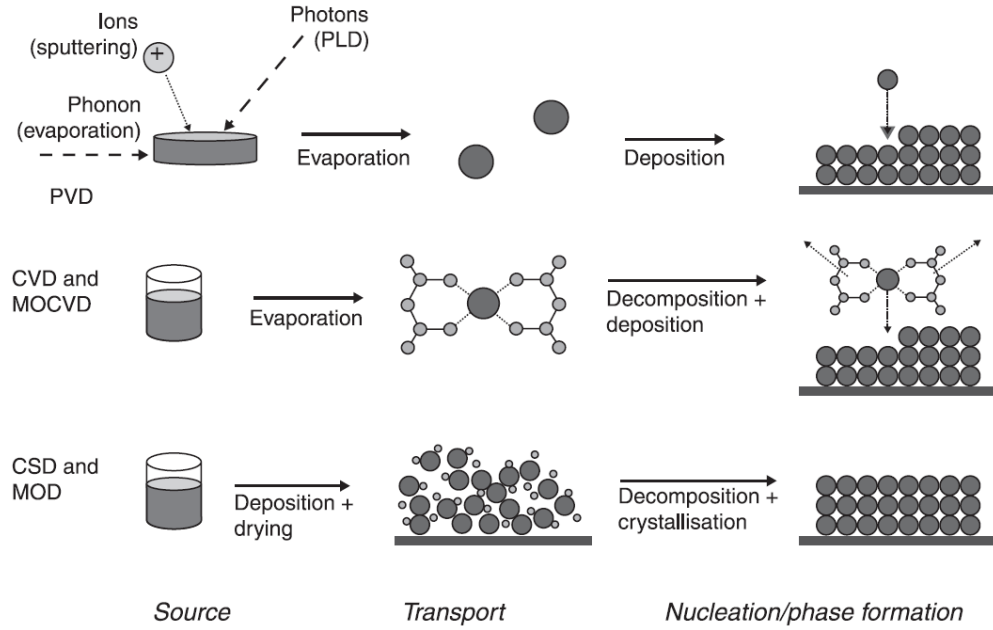


Figure 1-13. Schematic of process of deposition for PVD, CVD/MOCVD and CSD/MOD.

1.4. Critical current enhancement of REBCO.

As shown in figure 1-14, tremendous progress has been made in improving the critical current capability of HTS wires to make them viable for applications. REBCO due to high irreversibility field, better phase stability, high crystalline quality, lower surface resistance, lower anisotropy, and absence of poisonous elements that are present in Hg, Tl or As containing compounds are preferred over other HTS conductors for in-field applications. As can be seen in figure 1-14, several companies like SUNAM, Superpower, AMSC, Fujikura, are making long lengths of undoped and doped REBCO films on flexible substrates with critical current over 280 A/12 mm at 77 K self field. REBCO coated conductors are the only superconductors which have wide spread applications over broad range of temperature (77 K – 4.2 K) and a wide range of fields (0 – 20 T and above). Several applications like high energy particle accelerators, fusion reactor magnets, motors, generators, superconducting magnetic energy storage, and magnetic resonance imaging are

possible due to their high critical temperature, high irreversibility field and high critical current density [56–64].

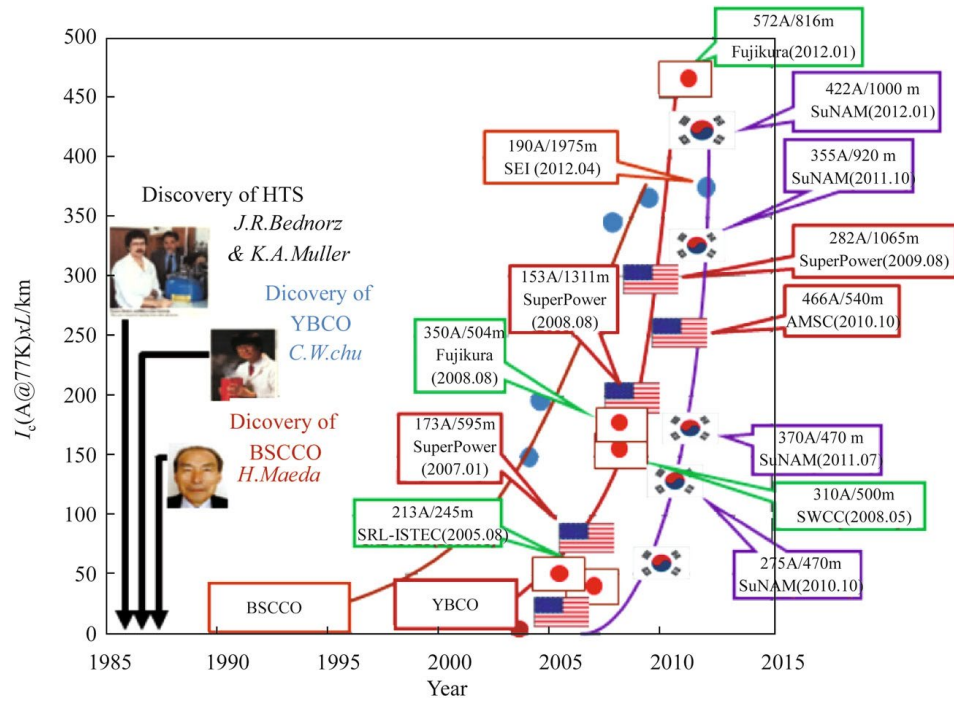


Figure 1-14. History of research and development of HTS wires.

However, the desired rapid and wide range usage of REBCO is limited due to its high cost when compared with other superconductors. For example, at 4.2 K, NbTi costs ~ \$1/kA-m and Nb₃Sn ~\$8-10/K A-m, while REBCO costs 10 times higher (~ \$100/kA-m) than Nb₃Sn [66,67]. (dollars per kiloampere × meter (\$/kA×m) is the figure-of-merit for comparing costs of different electrical wires at a specific operating point). Reducing cost of REBCO is the only possible way to make it feasible for applications. Cost can be reduced by (a) improving the engineering current density (J_e) of these superconductors and (b) reducing the wire cost. Improvement of J_e [I_c /total cross-sectional area (including copper stabilizer (40 μm) and Ag layer (3 μm))] can be interpreted as improvement in the critical current (I_c) of REBCO. The critical current of REBCO can be improved in two different

ways by incorporating pinning centers or by increasing thickness without deterioration of J_c (critical current density $J_c = I_c/\text{cross-section of REBCO}$).

1.4.1. REBCO critical current enhancement – using pinning centers

As discussed earlier in section 1.2.2., vortices generated in mixed state of type-II superconductors can be immobilized by incorporating pinning centers in the REBCO matrix. Several researchers have shown that the in-field critical current of REBCO over a wide range of temperature and fields can be increased by adding dopants to form BMO [$M=\text{Zr, Hf, Sn}$] nanoscale defects which enhance flux pinning [46,48–50,68–77]. The enhancement of J_c and strong pinning in the magnetic field applied parallel to the c -axis by doping YBCO with 5 mol% BaZrO_3 (BZO) was first shown by MacManus et al. [47]. Goyal et al. [77] showed that BZO nanocolumns get self-assembled which can be grown through the whole film thickness in YBCO doped with 2 vol% BZO (Figure 1-15(a)). A significant increase in J_c has been shown in 2 vol% BZO doped films compared to an undoped film, when an applied magnetic field is parallel to c -axis ($B \parallel c\text{-axis}$). The magnetic field dependence of J_c and angular dependence of J_c at 77 K, 1T of both doped and undoped films are shown in figure 1-16 (b) and (c) respectively.

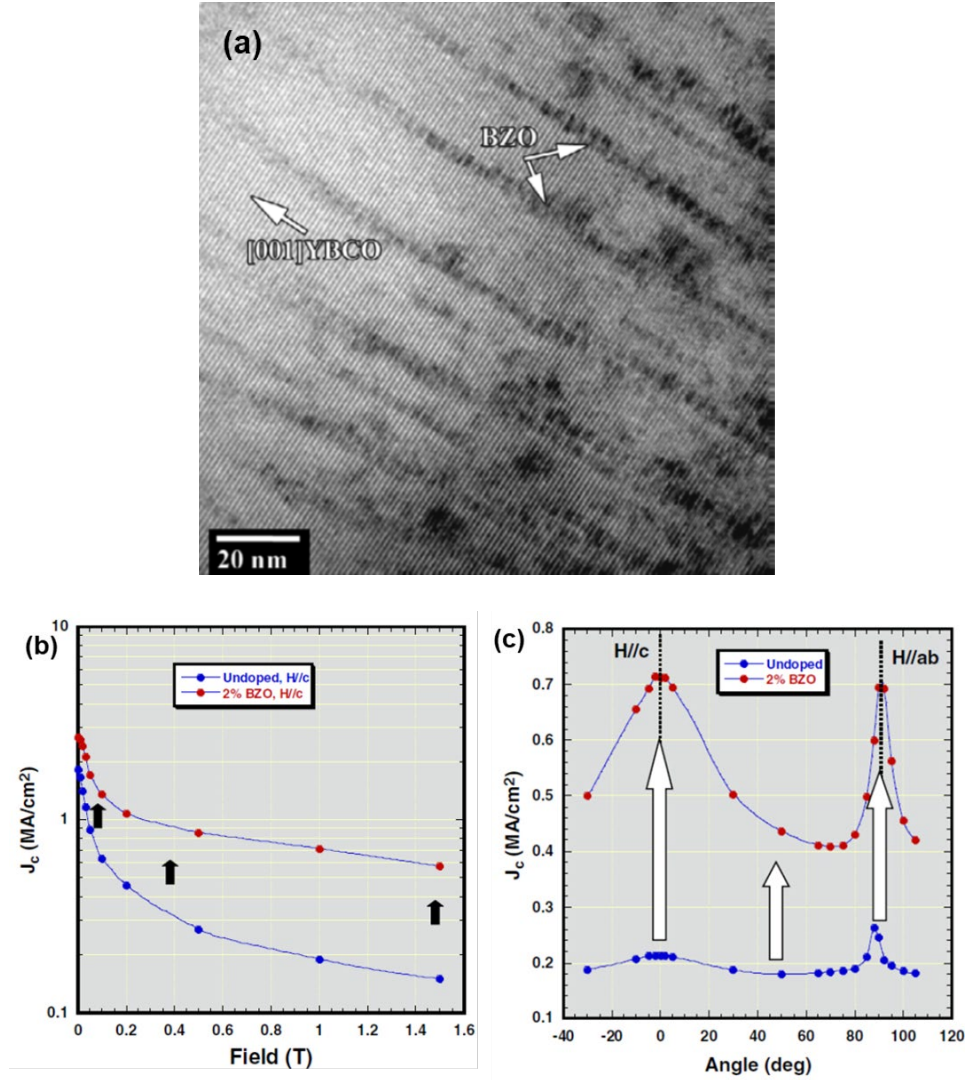


Figure 1-15. (a) TEM cross-section of 2 vol% BZO doped YBCO film, (b) J_c vs B of an undoped and a 2 vol% BZO doped YBCO films, (c) angular dependence of J_c at 77 K, 1 T of an undoped and a 2 vol.% doped YBCO films.

The reason behind self assembly of nanocolumns was proposed by Wee et al. [78]. The large strain-field developed due to lattice mismatch ($\sim 8\%$) between YBCO and BZO was proposed to be the driving force behind self-assembly of nanocolumns parallel to surface normal orientation. Until the matching field (field at which density of nanocolumns is equal to the number of vortices, $F_p = F_L$) is achieved, a single vortex gets pinned by an individual continuous nanocolumnar defect (its called as single vortex regime). Increasing

the applied magnetic field beyond the matching field, increases the number of vortices and the interaction between them. Beyond this point, vortices start moving and are collectively pinned by different pinning defects having size similar to ξ [79,80].

Coherence length of a REBCO film is dependent on the temperature as given below [81]:

$$\xi^2(T) = \xi^2(0) \left(\frac{1}{1 - \frac{T}{T_c}} \right). \quad (1-7)$$

Hence as the temperature changes, coherence length changes (vortex size $\sim 2\xi$), the number of effective pinning centers required to pin at different temperature also changes. Self assembled nanocolumns with diameter $\sim 2\xi$ show very strong correlated pinning along their growth direction (usually $B \parallel c$ -axis) at high temperature. However, as temperature changes, pinning by these defects become dominated by pinning centers like weak point pins. It has been reported in the literature that domination by weak point pins over correlated pinning starts at or below ~ 30 K [36,42,46,48,50,80–82]. It has been established that self-assembled nanocolumns might not provide the dominant pinning directly at lower temperatures, but a higher density of nanocolumns can increase the density of weak pins which are effective in pinning at lower temperatures [80]. Due to the higher lattice mismatch between BZO and REBCO matrix, increase in the density of nanocolumns induces more strain in the REBCO matrix and that increases the density of weak pins.

However, dopant concentration can be increased only to a certain limit after which it starts impeding the self field and in-field critical current density [83–85]. A higher density of nanocolumns reduces the volume of superconducting fraction and also results in deterioration of crystallinity of the REBCO matrix which leads to the decrease of self-field J_c and in-field J_c .

RE_2O_3 precipitates (random defects) are another pinning defect which have shown to increase self-field J_c and also in-field performance, especially in a-b plane orientations [86,87]. The in-plane lattice mismatch between RE_2O_3 and REBCO is low ($\sim (2-3)\%$), due to which a large lattice distortion is not created. However, a high density of RE_2O_3 can disturb the REBCO lattice. Hence, it is necessary to optimize the pinning landscape according to the required temperature and field of application.

1.4.2. REBCO critical current enhancement by increasing thickness

Increasing the REBCO thickness without suppressing the self-field critical current density and the film's microstructural properties is a direct way of further increasing the critical current carrying capability of REBCO. However, making thicker REBCO had not been a straightforward path due to several complexities involved in maintaining consistent process control to get a homogeneous film above 2 μm . Degradation of self-field J_c with increase thickness had been seen consistently in REBCO, independent of the deposition technique involved, as shown in figure 1-16 [65].

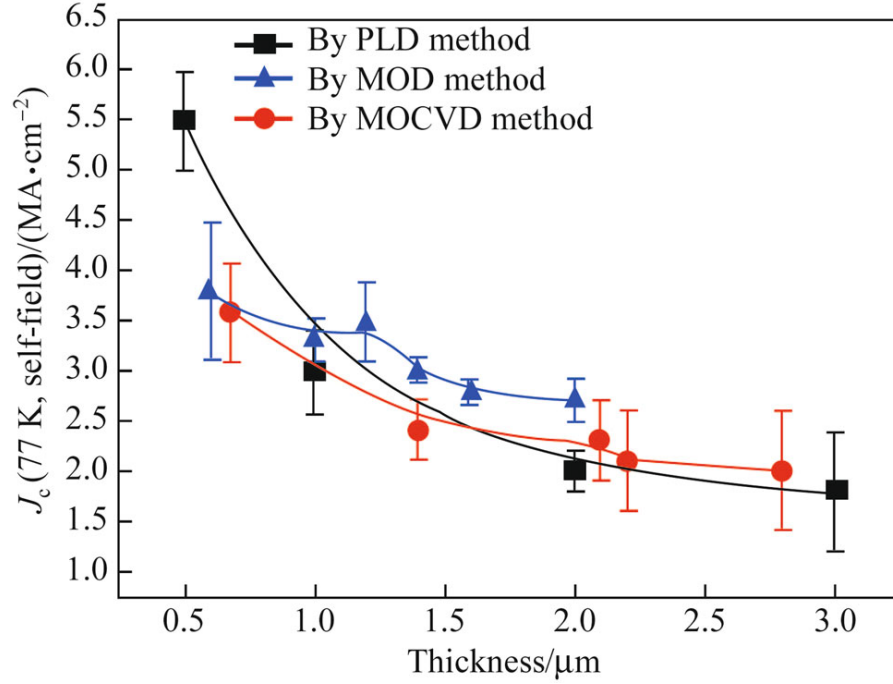


Figure 1-16. Thickness vs 77 K self-field J_c of REBCO grown by PLD, MOD and MOCVD.

In 1993, Foltyn et al. showed their experimental results of depositing REBCO film upto 6.4 μm thick on single crystal substrates using PLD [88]. They showed a sharp decrease in 77 K self field J_c with film thickness increasing from 0.2 to 1 μm as measured. Further increasing REBCO film thickness to 6.4 μm showed lesser effect on J_c and J_c saturates near $1\text{MA}/\text{cm}^2$ [88]. Crystalline degradation with increasing film thickness was thought to be the reason behind the above behavior in self field J_c .

In 1999, another work was presented by Foltyn et al., showing the experimental result of depositing thicker films on flexible metal substrates [89]. Degradation of J_c was observed both near substrate and above 2 μm . It was reasoned that the lower J_c near the substrate is due to impurity diffusion across the buffer, as the substrate is exposed to higher temperature for a longer deposition time to deposit thick REBCO. For a film with thickness above 2 μm , it was shown that the dominant orientation of grain changes from c -axis to a -

axis which acts as a deadlayer and blocks the flow of current. To avoid this microstructural degradation, a multilayer architecture of YBCO and CeO₂ has been shown to achieve a J_c of over 1000 A (figure 1-17) [90,91]. Although this is a remarkable improvement in J_c , this architecture complicates the deposition process while increasing the cost. Also, this type of architecture depletes the pinning effectiveness of nanocolumnar defects, which plays an important role in maintaining high J_c at applied fields. Hence, improving critical current capability of REBCO as a single layer is a better approach.

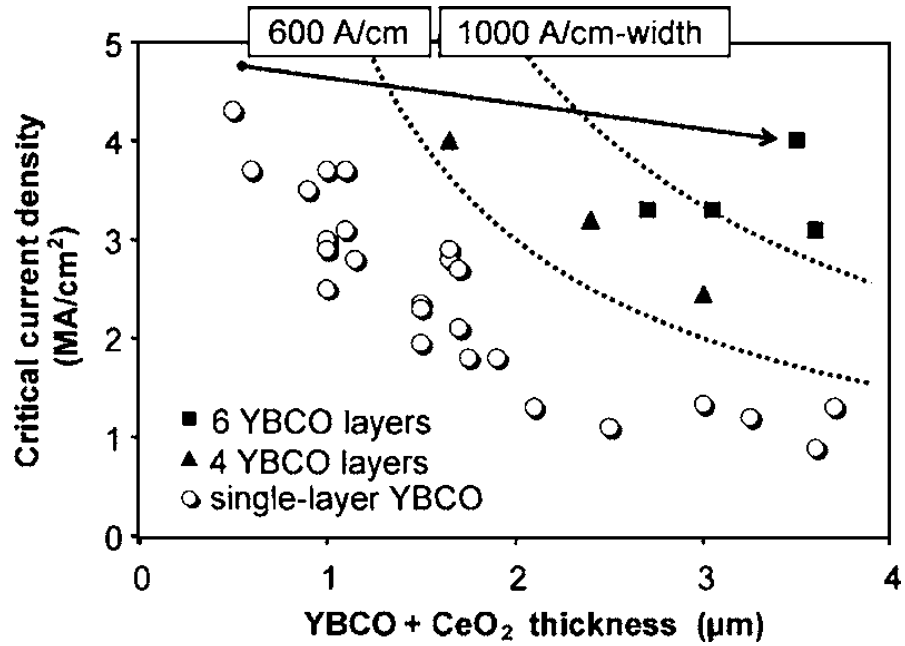


Figure 1-17. Comparison of thickness dependence of 77 K self field J_c for single layer YBCO and multilayers (YBCO/CeO₂).

Major reasons for the degradation of self-field J_c in single layer REBCO have been proposed as the formation of misoriented *a*-axis oriented grains, oxygen vacancies, non-homogeneous growth, formation of secondary phases, increase in grain size and boundaries with thickness, the occurrence of voids, etc. [33,65]. In 2009, Zhou et al. showed the microstructure evolution with increasing thickness of 5 mol% BZO and 5 mol% Y₂O₃

doped (Gd, Y)BCO grown on single crystal substrate as shown in Figure 1-18 [92]. It was reported that with doping, 77 K self field, and in-field J_c did improve (compared to undoped YBCO) and no dead layer was formed. However, coarsening of grains and grain boundaries was certainly observed with increasing thickness, which is an impediment to self-field J_c (figure 1-18).

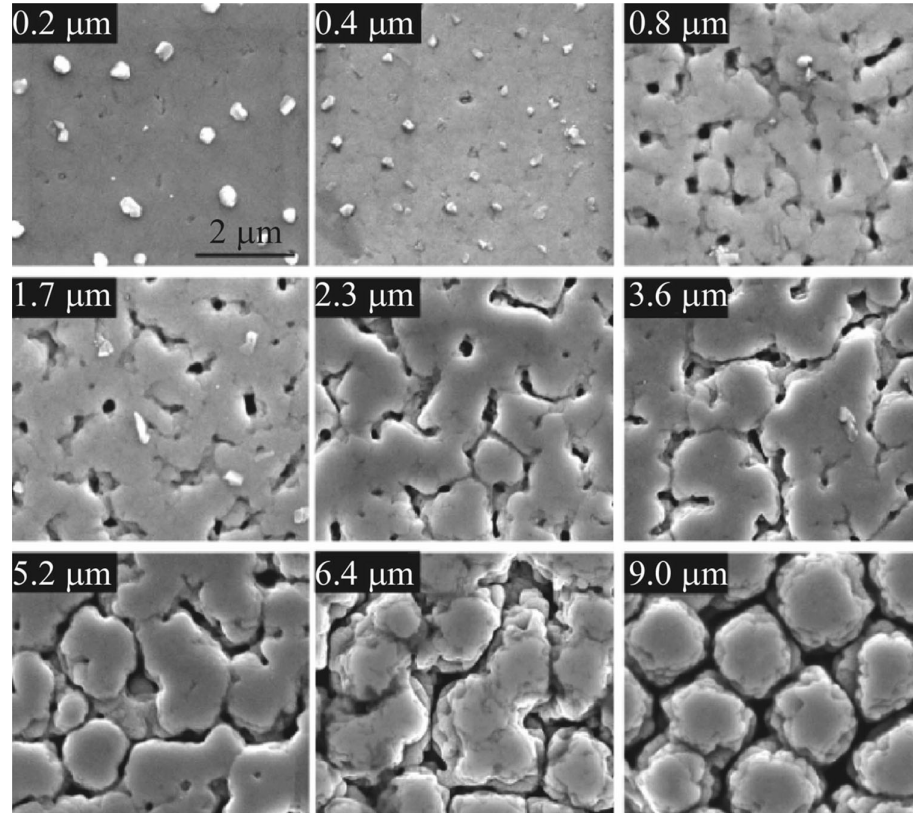


Figure 1-18. SEM images of the surface morphology of REBCO film different film thicknesses (0.2–9 μm) (the scale is the same for all the images).

Some of the recent developments in improving the performance of thick REBCO shows promising results. In 2014, Kim et al. showed a result of 77 K self field J_c of over 1500 A/cm in a 5 μm SmBCO film using the co-evaporation process and inclined substrate deposition [93].

Few other research groups have shown the development of thick REBCO (above 2.5 μm), using different techniques and substrates, to improve self-field critical current density and microstructure quality of these films [49,70,94–98]. However, these results are nowhere closer to getting the true benefit of thick REBCO films. Also, very limited or no information is available on growing thick REBCO films with elongated nanocolumns to achieve high in-field performance, required for practical applications.

This had been the motivation behind the research done for this dissertation. An advanced Metal Organic Chemical Vapor Deposition (A-MOCVD) system has been used to grow 3.5 – 5 μm doped and undoped (Gd, Y)BCO films to achieve record high performance at 77 K self field, high temperatures (65 K), lower field (0.25 T and 1.5 T) and low-temperature (50 K -4.2 K), high fields. The pinning landscape of these thick (Gd, Y)BCO tapes has been studied and optimized to provide high performance at the required temperature and fields. Also, work has been performed to increase the precursor-to-film conversion efficiency of reactants to further reduce the production cost.

Chapter 2. Experimental methodology

This section presents a detailed description of the pre-deposition preparation, deposition method and post deposition procedures including characterization involved in analyzing thick REBCO (doped and un-doped (Gd, Y)BCO). Pre-deposition preparation includes buffer tape preparation and liquid precursor preparation. REBCO is fabricated under vacuum using advanced metal organic chemical vapor deposition system (A-MOCVD). Post-deposition treatments includes silver sputtering and oxygenation of the thick REBCO film. Finally the electromagnetic and materials characterization techniques used for the REBCO coated conductors are illustrated.

2.1 Pre-deposition preparation

This section involves the preparation of precursor and buffer tapes for the deposition of REBCO using Advanced Metal Organic Chemical Vapor Deposition (A-MOCVD).

2.1.1. Buffer tape preparation

REBCO is deposited on biaxially textured 12 mm wide Hastelloy/ Al_2O_3 / MgO / LaMnO_3 . The schematic illustration of different layers of REBCO coated conductor with buffer stack, silver and copper layer as shown in Figure 2-1 [99,100]. The buffer used for REBCO deposition has five different layers (Al_2O_3 , Y_2O_3 , IBAD MgO , Homo-epitaxy MgO , LaMnO_3) in between 50 μm Ni-based C-276 Hastelloy substrate and REBCO film.

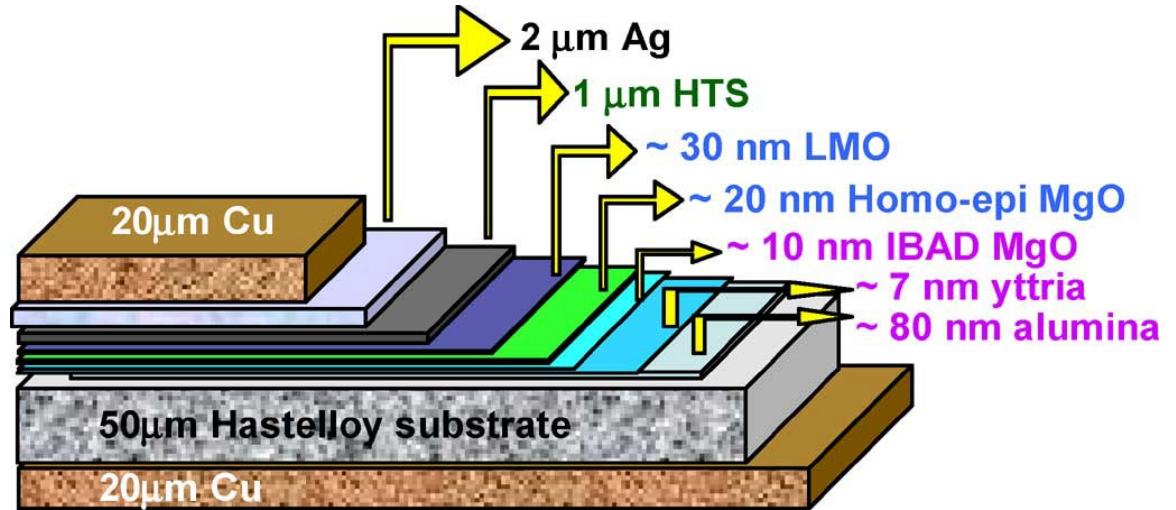


Figure 2-1. Schematic illustration of buffer layers used for REBCO deposition.

Description of each layer is given below:

- (1) Hastelloy substrate: C-276 hastelloy is used as the base substrate with a thickness $\sim 50 \mu\text{m}$. It is a nickel-based alloy with the following nominal composition (in weight %) of different elements: Nickel- 57 %, Chromium-16 %, Molybdenum-16%, Iron - 5%, Tungsten - 4%, Cobalt - 2.5% max, Vanadium - 0.35%, Manganese - 1% max Mn, Silicon - 0.08% max, Carbon -0.01% max, and copper – 0.5 % max. Hastelloy C-276 has a good mechanical strength and flexibility with a high melting temperature of 1350°C [101].
- (2) Al_2O_3 layer : Thickness of this layer $\sim 80 \text{ nm}$ and it is deposited at room temperature. This layer acts as diffusion barriers to any metal ions from the substrate [99]. Since the deposition temperature of REBCO is very high, there is certainly a possibility that some of the elements from hastelloy can diffuse into REBCO which will destroy its superconducting properties.

- (3) Y₂O₃ layer: This layer is ~ 7 nm thick and is deposited by sputtering at room temperature. It serves as a seed layer to help IBAD MgO nucleation [99].
- (4) MgO layer: It is deposited by IBAD at room temperature and is ~ 10 nm thick. This is the key layer which forms biaxial texture and provides a template for epitaxial REBCO deposition.
- (5) Homo-epitaxial MgO layer: This layer ~ 40 nm thick and is deposited to provide robustness to IBAD MgO and helps improving the texture.
- (6) LaMnO₃ (LMO) layer: This layer acts as a cap layer and is ~ 50 nm thick. It has a good lattice match with YBCO. The lattice parameter of MgO, LMO and YBCO are 4.21 Å, 3.88 Å and 3.86 Å respectively [100,102,103].
- (7) REBCO layer is deposited using A-MOCVD and is described in section 2.2.
- (8) Ag layer: (2-3) µm of silver is deposited on top of REBCO using sputtering techniques. This layer is required for good electrical contacts to the superconducting film and transfers current from superconductor layer to copper layer in case of any local hot spot or defect in the REBCO film.
- (9) Cu layer: This is the last layer, which gets deposited on top of silver layer, using electrodeposition technique. Thickness ~ 20 µm thick on each side. This layer serves as a stabilizer layer and provides an alternate current path.

These buffer layers were cut into multiple pieces each 65 cm long and spot welded with 56 cm of leader tape (unpolished hastelloy) in between. Having multiple buffer tapes with leader tape in between, allows processing REBCO films with different parameters (both process and chemical compositions) to optimize conditions and compositions for a target application. Spot welding of these tapes together is very crucial since slight

misalignment along width of the tape can make these welded tapes stick in the specifically designed rollers of the A-MOCVD. These welded tapes were rolled in to a spool and loaded in A-MOCVD for REBCO deposition process.

2.1.2. Liquid Precursor Preparation

Precursor for REBCO deposition in A-MOCVD was prepared inside a glovebox using THF (tetrahydrofuran) as a solvent and organometallic compounds of the elements required for REBCO deposition. Depending upon the elements of the superconductor to be prepared, the chemical compounds of Y(TMHD)_3 , Gd(TMHD)_3 , $\text{Ba(TMHD)}_2(\text{phen})_2$, Cu(TMHD)_2 , Zr(TMHD)_4 and Hf(TMHD)_4 were added in tetrahydrofuran (THF) at an appropriate mole ratio. All these compounds were in powder form and were procured from STREM Chemicals and Sigma Aldrich. They were stored and prepared in an inert environment inside a glove box. Each compound was weighed in grams with a precision of 0.001 g. The calculation of the exact mass of each compound was calculated based on the molar concentration (solute moles per liter of solvent) of solution and the specific molar ratios of each element to be used.

Sample calculation for the preparation of 700 ml precursor solution at 0.025 Molarity with molar ratios (or compositional ratios) of Gd:Y:Ba:Cu :: 0.65:0.65:1.97:2.60 and 5 mol% Zr as dopant is given below.

Molarity of solution – 0.025 M.

Total number of moles of solute (n_{total}) = $0.025 \text{ (moles/liter)} \cdot 0.7 \text{ (liter)} = 0.0175 \text{ moles}$

Total molar ratios (or compositional ratio) = $0.65 + 0.65 + 1.97 + 2.60 = 5.87$

Moles of individual element (example- for Yttrium) (n_Y) = $\frac{0.65}{5.87} \times 0.0175 \text{ moles} = 0.0019378 \text{ moles}$

The number of moles of each individual element is then multiplied by the formula weight of its TMHD compound to get the weight to be added in the solvent.

Formula weight of $Y(TMHD)_3 = 638.71 \text{ grams/moles}$

Amount of $Y(TMHD)_3$ to be added = $0.0019378 \text{ moles} \times 638.71 \frac{\text{grams}}{\text{moles}} = 1.238 \text{ grams}$

Similarly, masses of $Gd(TMHD)_3$, $Ba(TMHD)_2(phen)_2$, $Cu(TMHD)_2$ gets calculated as shown in table 2-1.

Since Zr is added as a dopant, it is not included in the calculation of the total moles value. The moles of Zr is calculated as = $\frac{0.05}{5.87} \times 0.0175 \text{ moles} = 0.000149 \text{ moles}$.

Table 2-1. Amount of solute to be added in 700 ml of THF solvent at 0.025 M.

Compound	Mass of solute (in grams)
$Zr(TMHD)_4$	0.123
$Gd(TMHD)_3$	1.370
$Y(TMHD)_3$	1.238
$Ba(TMHD)_2(phen)_2$	5.078
$Cu(TMHD)_2$	3.333

Once all the solutes were added to the solvent, the precursor was left for magnetic stirring inside a glovebox for at least 3 hours to dissolve all solutes completely. The precursor solution was then loaded in steel precursor containers inside the glovebox and then loaded to A-MOCVD setup for precursor supply. The precursor was at no time exposed to air or moisture to avoid any unwanted chemical changes.

2.2. REBCO deposition using Advanced Metal Organic Chemical Vapor Deposition

2.2.1 A-MOCVD reactor parts description

All REBCO films were deposited using cold-wall type reel-to-reel advanced MOCVD reactor (A-MOCVD). Figure 2-2 shows details of the parts of A-MOCVD reactor used for depositing REBCO films presented in the result section. Figure 2-2 (a) shows a reel to reel A-MOCVD reactor, tape starts from the left spool, goes through deposition chamber and end in right spool (collecting spool). All tapes were deposited in stationary conditions and then moved out to go to the next buffer tape for another deposition. The exhaust section of A-MOCVD is divided into two main sections: Deposition zone exhaust and main chamber exhaust. The deposition zone exhaust has two side zones and one main zone (middle) which are separately controlled by two different throttle valves and different gate valves. The main chamber exhaust has a separate throttle valve and a gate valve for controls. All these different exhaust sections are connected to one main exhaust pipe which then connects to a dry pump with a final main gate valve.

Figure 2-2 (b) shows the precursor and carrier gas delivery system. Once the precursor is prepared inside glovebox, the stainless steel containers (shown in figure 2-2 (a), named A,B,C,D,E) were cleaned with acetone, purged with argon in the glovebox antechamber (to remove moisture and any other impurities), and then taken inside the glovebox to fill with the prepared precursors. Precursors were filled carefully into these containers (except one which was filled with pure THF) and then all valves of the containers were closed, to avoid any contact with air. These containers with liquid precursors and THF were then loaded on the frame as shown in Figure 2-2 (b). These

precursor containers were connected to helium gas (inert gas) line, which pressurizes the liquid precursor stored inside the steel containers. The pressure of helium gas was controlled by regulators and kept at 5.2 bar. Once the liquid precursor contained in the precursor containers were pressurized, the outlet valve of these containers was opened to allow liquid precursor to flow through inline filters (filter mesh size - 15 μm), which can trap any deposit above 15 μm , which if not used, can clog liquid MFC or injectors present in the evaporator. Through inline filters, liquid precursor travels to an automatic precursor changer that has 5 inlet ports and one outlet port. These 5 inlet ports were connected to different stainless steel container carrying precursors with different compositions. It allows us to use different precursors to test different compositions in the same experiment. Also, this controller has the capability of switching time in milliseconds, which prevents any interruption in the flow during the deposition. This is very important, as with little delay, a bubble can get formed inside the liquid precursor delivery tube, which affects the flow of precursor and hence ruins the deposition. Selected liquid precursor from the automatic precursor changer goes to liquid MFC (mass flow controller) (figure 2-2 (b)). Liquid MFC is used to control the flow of liquid precursor with precision of two decimal units. The liquid precursor flow rate can be changed according to the required parameters for the experiment but generally it was kept at 4 ml/min. The liquid precursor travels to the inlet of the evaporator as shown in Figure 2-2 (b). In Figure 2-2 (b), nitrogen was used as a carrier gas that flows through indicated carrier gas line. Pressure of carrier gas as controlled by using the shown regulator (shown in Figure 2-2 (b)) and pressure was maintained at 4 bar. Next to the pressure regulator, is the gas MFC which controls the flow carrier gas to

the evaporator. Flow of carrier gas can be changed depending on the type of experiments but generally flow is around 483 sccm.

Figure 2-2 (c) shows evaporator that receives carrier gas and precursor liquid from the outlet of carrier gas MFC and liquid MFC (mentioned in Figure 2-2 (b)). Liquid precursor gets delivered to the liquid injector, which operates at an optimized frequency and converts liquid precursor into mist form. These liquid injectors have very small holes at its outlet. Next to liquid injector, is a mixture injector. At the inlet of mixture injector, liquid precursor in mist form gets mixed with carrier gas (nitrogen) and is transferred to heated vaporizer. Mixture injector also works at an optimized frequency and injects the mixture of carrier gas and precursor mist inside the heated vaporizer. Vaporizer has three different heating zones which are maintained at ~ 270 - 280 °C, to convert this precursor (mist form) and carrier mixture into vapor form. All elements of precursor and THF have vaporizations temperature lower than 260 °C. This evaporator is connected to the main reactor chamber of the A-MOCVD, which is at vacuum during the deposition process. Vacuum helps transfer the vaporized precursor to the reaction zone. Every part of the vapor path (from evaporator to inlet of reaction zone) was maintained at ~ 270 - 280 °C, to avoid condensation of any element. The entire vapor path is divided into seven tape heater zones, each of these have one controlling thermocouple and at least two monitoring thermocouples. Heating of these heater zones were controlled by solid state relays and PID closed loop controls. In the vapor path, high-purity oxygen gets mixed with vaporized precursor and carrier gas mixture before entering the inlet of reactor, as shown in Figure 2 (d). Precursor flows in the direction perpendicular to the tape in between two heated plates (top and bottom plates) with channel height “h”. Both top and bottom plates were heated

using strip heaters (250 W, 120 V) connected in parallel. Top plate had three different process heater zones, each of these have separate controlling thermocouples which were connected in closed loop with solid state relays and controlled using optimized PID controls. Bottom plate had four separate zones, each of which are heated and controlled separately, similar to top plate. Temperature of all zones in top and bottom plate was maintained $\sim 270\text{-}280^\circ\text{C}$. The height “h” mentioned in the figure 2 (d), can be changed with different height of the top plate insert used, which is useful in increasing precursor-to-film conversion efficiency that will be discussed in the result section. Substrate tape was situated in the recessed channel with an optical probe located underneath the tape to monitor tape temperature directly. Quartz was placed in between the optical probes and substrate tape in order to avoid deposition on optical probes and to restrict flow from holes provided for optical probes in the bottom plate. Figure 2-2 (e) shows the non-contact tape heating used in A-MOCVD reactor. Optimized current was supplied through the substrate tape from specially designed rollers (Figure 2-2 (e)). Tape gets heated with its own resistance as shown in Figure 2-2 (e) and (f). Tape should be kept floating in between the rollers, since any contact of tape with quartz or any part of the bottom plate will allow distribution of current, leading to non-uniform heating of the tape. A 2.0 kg tension was applied on the tape to keep it stable and floating. The deposition zone length is 32 cm. Optical probes situated beneath the tape monitors infrared emissions from the tape to provide the temperature of the tape. Optical probes were calibrated earlier using data from thermocouple welded on the heated substrate tape to avoid large variation in absolute values. Also, vertical dispersers were used to maintain flow uniformity along the length of

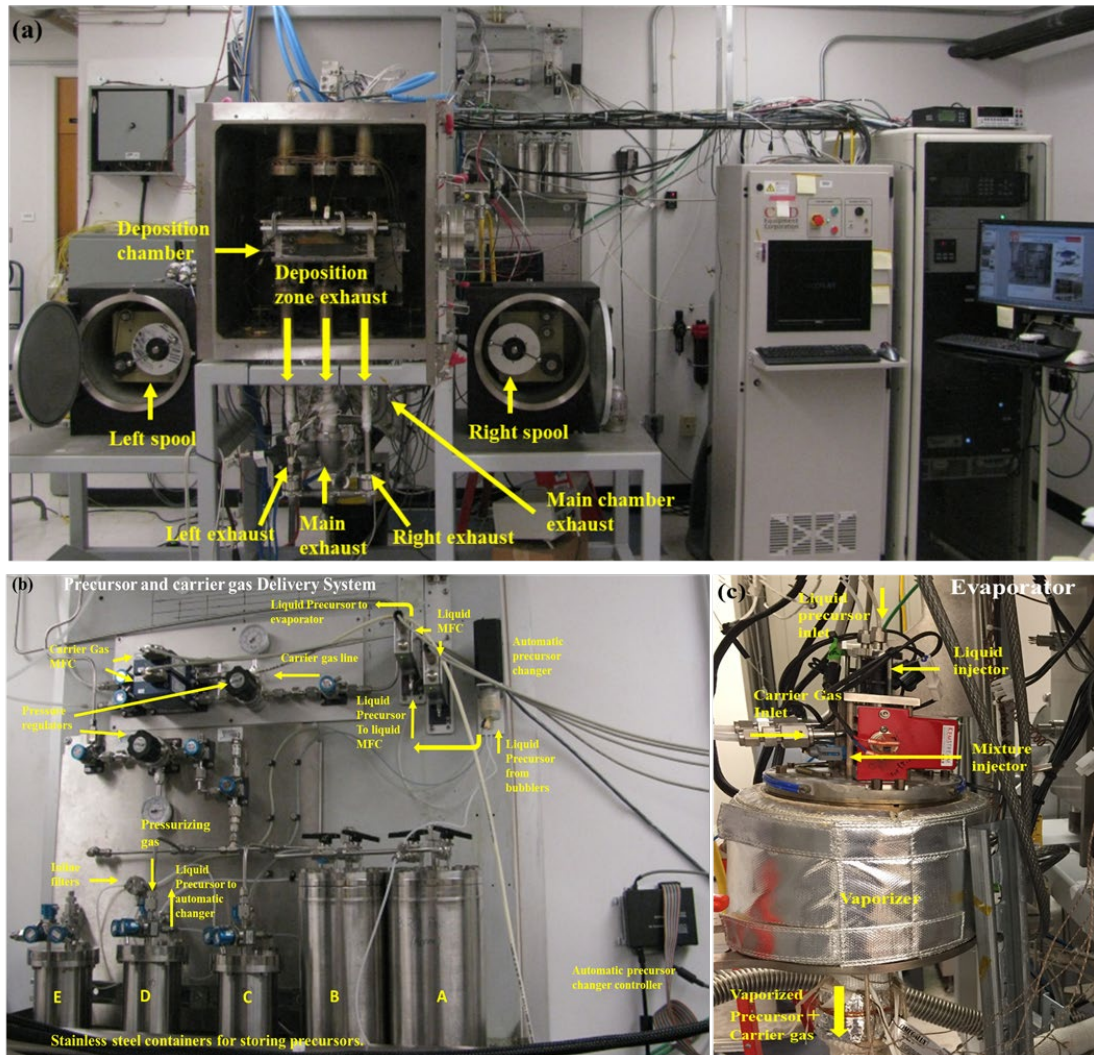
the tape (Figure 2-2 (e)). As shown in Figure 2-2 (e), three pressure sensors (indicated as A, B, C) were kept on bottom plate near exhaust to monitor pressure during deposition.

2.2.2. Deposition process

Once the spools were loaded in the A-MOCVD reactor, the doors of the spools and the reaction chambers were closed. Main gate valve was opened and throttle valve of main (middle) exhaust in the deposition exhaust zone was kept at 5%. A dry pump starts to keep all zones of the reactor under vacuum. Once pressure reduces below 0.50 Torr, all gate valves (side and main chamber) were opened and all throttle valves (sides and main chamber) were opened to 100 %. Once a base pressure of 0.30 Torr was achieved, all zones were heated to 270-280 °C. After all zones reaches the setpoint temperature, main chamber gate valves and throttle valves were closed to avoid any cross flow between deposition chamber and main chamber. THF, carrier gas and oxygen were flown for 30 min to stabilize all temperatures and maintain a constant flow. Throttle valves of main (middle) and side channel of deposition exhaust system were opened to maintain 1.90 Torr deposition pressure. Then, the first substrate tape was moved to the deposition zone and heated to the required temperature while supplying the optimized current. Once the tape was heated, the mixture of vaporized precursor, carrier gas and oxygen, goes over the heated substrate tape and the REBCO film is epitaxially deposited on biaxially-textured LaMnO_3 . During tape heating, as the REBCO thickness grows, the change in emissivity from back side of substrate sensed by optical probes gets compensated with increase in current to maintain the same temperature across the whole REBCO thickness (Figure 2-2 (g)). As can be seen in Figure 2-2 (g), the temperature is maintained at constant setpoint value by compensating

the change in emissivity with increase in current and hence power. After the film was deposited for the required amount of time, liquid flow was switched back from precursor to THF and temperature of substrate was reduced to 0 °C. The same procedure was followed for all tapes fabricated in the experiment. After deposition, by-products and partially-decomposed precursor are removed from exhaust, where an oxygen sensor was placed to measure the residual oxygen concentrations after deposition.

After deposition of the last tape, THF was flown for 30 min to clean up injectors of evaporators and then whole reactor is cooled to remove the deposited tapes for post processing.



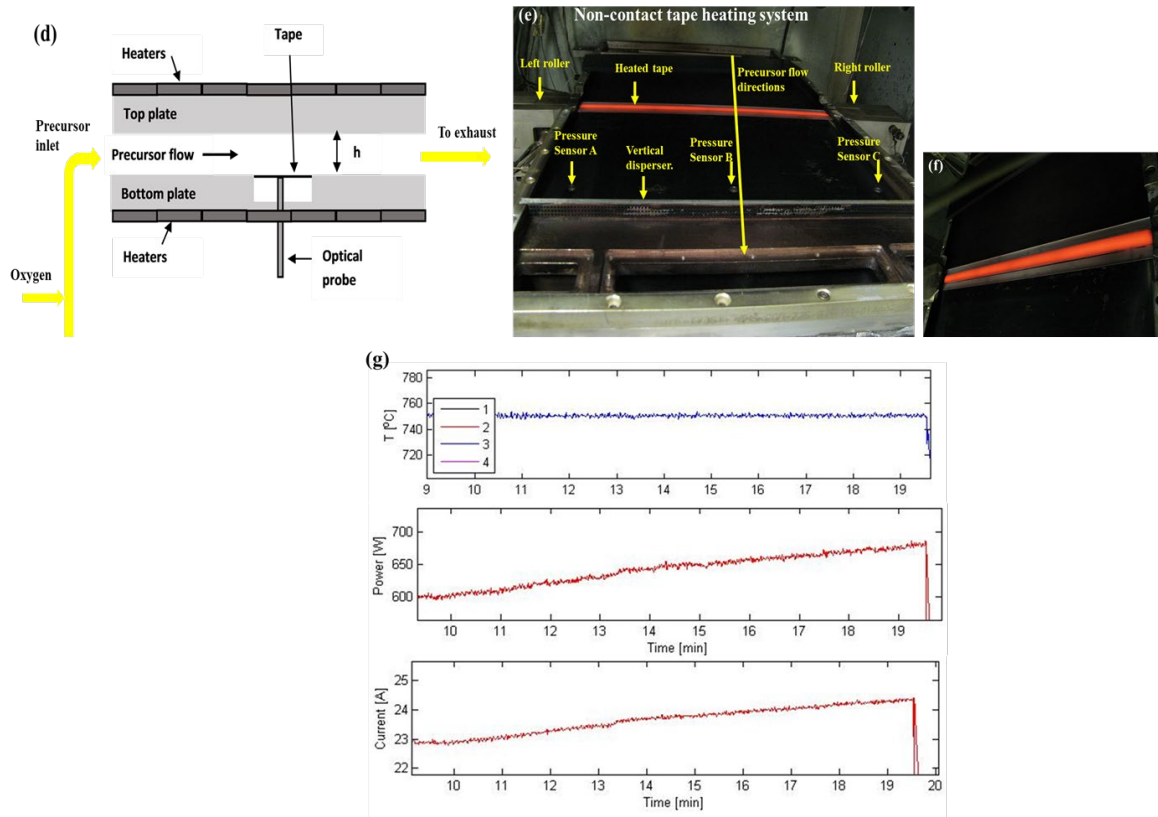


Figure 2-2. (a) Reel to Reel A-MOCVD system, (b) precursor delivery system, (c) Evaporator, (d) A-MOCVD schematic, (e) Tape heating system, (f) Heated tape (g) Temperature, power and current plot during REBCO deposition.

2.3. Post REBCO deposition process – Silver sputtering and oxygen annealing

Once the REBCO deposition was done, all samples were marked and taken for reel to reel silver sputter depositon using a DC magnetron silver sputtering system (Figure 2-3). The silver sputtering chamber was pumped down using roughing and turbo pump to a pressure of 3×10^{-6} Torr and then argon gas (~ 75 sccm) is supplied. Throttle gate valve was adjusted to maintain chamber pressure of 3×10^{-2} Torr and then plasma power supply was turned on (~ 800 W). The tape speed was maintained at ~ 7 cm/min to obtain $\sim 2 \mu\text{m}$

thickness on top of REBCO. Approx 0.5 μm silver was deposited on the back side of the tape.

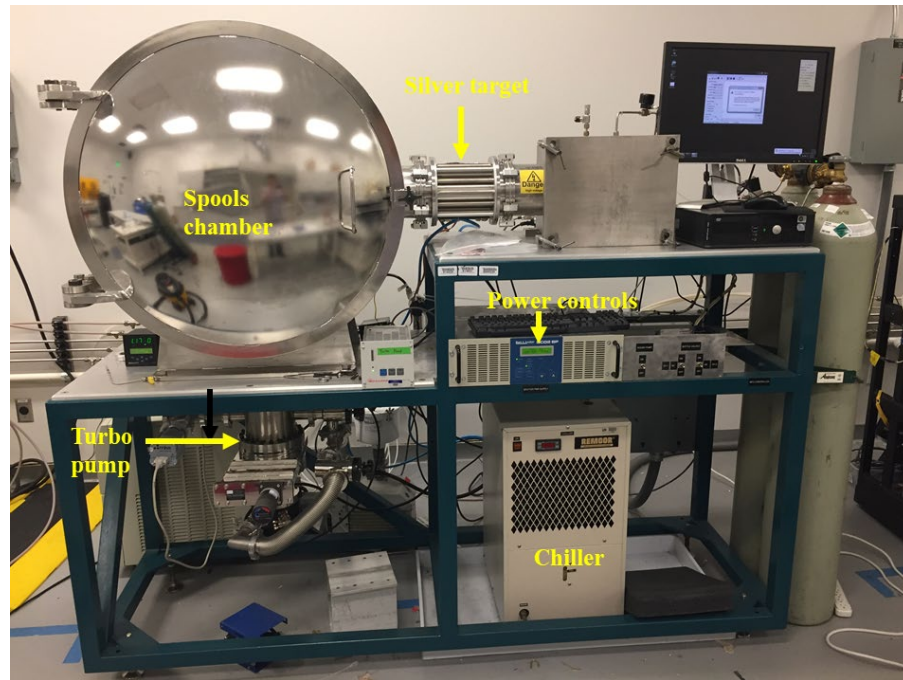


Figure 2-3. Reel to Reel silver sputtering system.

Silver sputtering was followed by oxygen annealing of sputtered REBCO tape. REBCO before annealing is in tetragonal form, which is non-superconducting due to insufficient oxygen. After oxygen annealing, REBCO transforms from tetragonal to orthorhombic structure and becomes superconducting. Figure 2-4 shows the horizontal tube furnace used for oxygen annealing. All samples were rolled in spiral form and kept on an Inconel tray inside the furnace for annealing. The temperature was increased to 500 $^{\circ}\text{C}$ at a ramp rate of 180 $^{\circ}\text{C}/\text{h}$ and held there for 2 hours. The samples were then cooled to room temperature with a ramp down rate of 180 $^{\circ}\text{C}/\text{h}$. Ultra high pure oxygen gas at 70 sccm flow rate was used. These samples were then taken out and cut for different types of electromagnetic and material characterization.

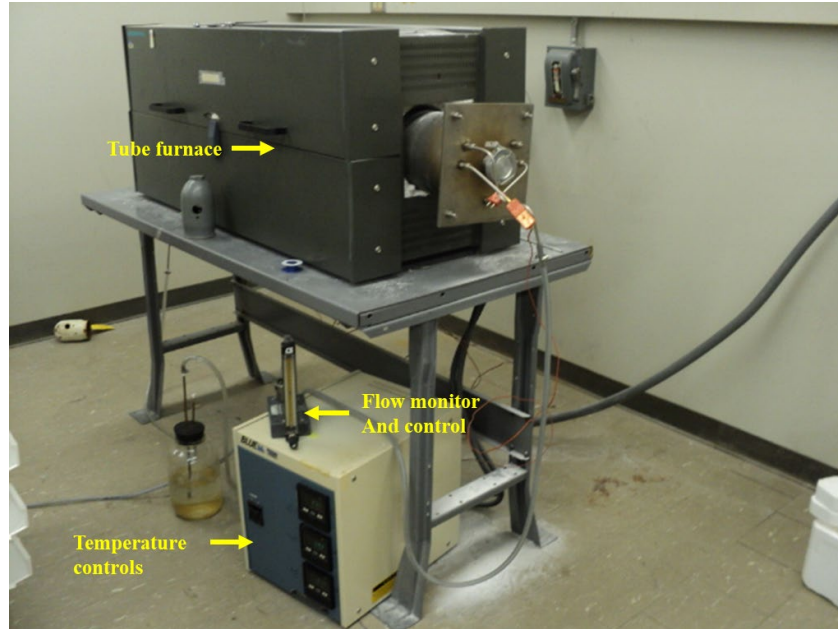


Figure 2-4. Horizontal tube furnace for oxygen annealing of REBCO.

2.4. Electromagnetic characterization of thick REBCO coated conductors

Different electromagnetic characterization techniques such as transport I_c measurement, In-field transport I_c measurement, In-field magnetic I_c measurement and critical temperature (T_c) were used to characterize the deposited thick REBCO coated conductors.

2.4.1. Transport self field and transport in-field I_c measurement.

Transport self field I_c and in-field I_c were measured using standard four-probe method and I_c is calculated using $1 \mu\text{V}/\text{cm}$ criterion. Indium solder (melting point $\sim 157^\circ\text{C}$) is used to make current and voltage contacts for the four probe measurement. Due to lower melting point of indium, no damage occurs to REBCO, since the heat generated while soldering is small.

2.4.1.1. Transport self field I_c measurement

One of the major issue in doing transport critical measurements of REBCO films is joule heating, which occurs once the tape becomes resistive and can cause damage to the sample due to drastic local temperature rise. With thicker REBCO film tape carrying more than 1500 A (in some cases), it is difficult to measure I_c across the full tape width. To avoid this problem, a bridge of width ~ 1 mm was prepared for transport I_c measurement. A 5.5 cm REBCO sample was patterned using kapton tape, with bridge width and length of ~ 1 mm and 10 mm respectively. The sample was then dipped into the silver etching solution containing 50 vol% hydrogen peroxide (H_2O_2) and 50 vol% ammonium hydroxide (NH_4OH) until the patterned bridge etched away. After removing silver, sample was washed with tap water and kept in REBCO etchant solution which contains 10 vol% diluted nitric acid. After REBCO was etched away and proper bridge is prepared, Kapton tape was removed and bridge measurement was done using microscope. For four probe measurement, both ends of the REBCO sample were soldered using indium to a pair of silver tapes (Lucas-Milhaupt, Fine Silver) present in the sample holder assembly. These silver tapes are attached to copper leads which are attached to current source. Voltage tabs are soldered using indium on top of sputtered silver. The distance between these voltage tabs were kept 4 cm apart. Now the entire assembly was inserted in a dewar filled with liquid nitrogen. Power supply was connected and a DC current as supplied using power source (Lambda, GEN-3300W 600 A) which flows through the entire sample and the voltage on the sample was detected using two voltage tabs that are directly soldered on the REBCO coated conductor. Voltage was detected by a two-channel nanovoltmeter

(2182 A, Keithley). A schematic illustration of four-probe method for transport critical current is shown in Figure 2-5.

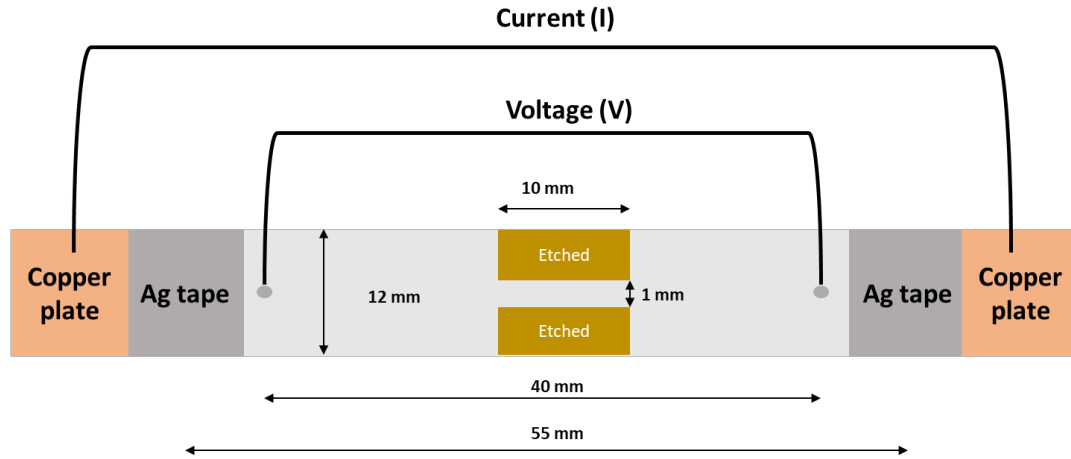


Figure 2-5. Schematic illustration of four-probe method for transport critical current measurement.

2.4.1.2. Transport in-field I_c measurement.

Transport in-field I_c measurements on REBCO film was performed in a custom-built electromagnetic system that can operate in a wide range of temperature (4 – 77 K) and magnetic field (0 – 9 T). Schematic illustration of this cryogenic system is shown in figure 2-6. It consists of three parts: Probe, control systems and cryostat. The probe consists of a rotating sample stage at one end on which the sample is mounted. The other end of the probe has a rotator which controls the sample stage movement and allows a rotation range of $\sim 200^\circ$. The control system has a nanovoltmeter (Keithley, Model: 2182A), power source (up to 600 A), and temperature controller (LakeShore, Model: 336). The cryostat consists of a superconducting magnet which can generate magnetic field upto 9 T, a cryocooler for cooling the system and a resistive heater for maintaining the required temperature. Helium is used as a cryogen in this system. The cryocooler condenses helium

gas into liquid helium and circulates it into the vessels, hence continuous supply of cryogen is not needed.

The same sample measured in liquid nitrogen as described in 2.4.1.1. is cut in between the voltage tabs and is used for measuring in this device at different magnetic field orientations and different range of temperature. As the current at lower temperature is higher than at 77 K, bridge of the transport I_c samples was narrowed down to $\sim 0.5\text{-}0.7$ mm in order to avoid any damage to the sample.

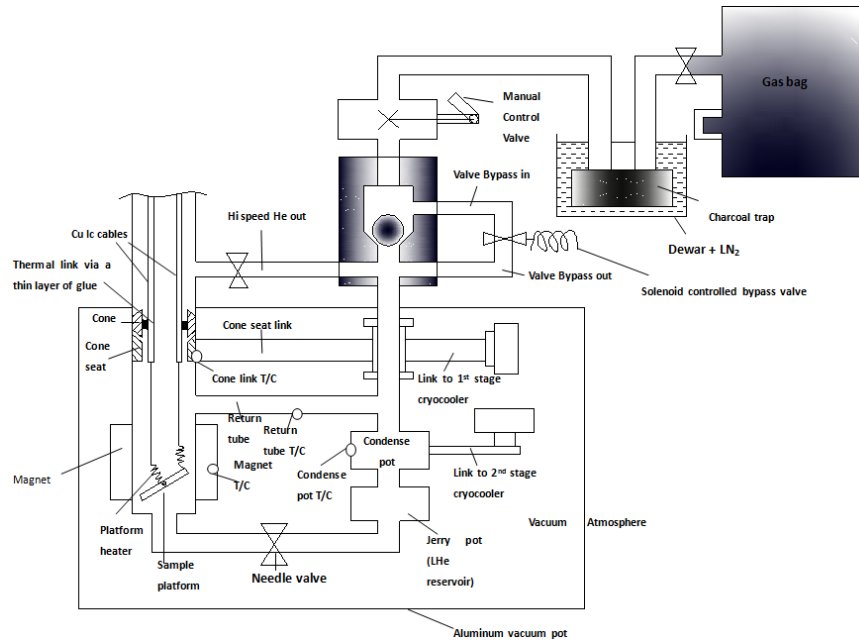


Figure 2-6. Schematic illustration of four-probe method for transport critical current measurement.

2.4.2. Magnetic in-field I_c measurement.

A Physical Property Measurement System (PPMS) was used to measure DC-magnetization while the magnetic field was swept at a constant rate of 100 Oe/s. A REBCO sample of size $3.5\text{ mm} \times 3.55\text{ mm}$ is loaded on the probe and magnetic field was applied

perpendicular to the tape. Measurements can be done over a range of temperature (77 – 4.2)K and magnetic field (0 – 13) T using this system.

Magnetic J_c can be determined from magnetization hysteresis loops by applying the extended Bean's model as shown below [104]:

$$J_c = \frac{20 \Delta M}{[a(1 - (\frac{a}{3b}))]}, \quad (2-1)$$

where ΔM is the width of the magnetization hysteresis loop (emu/cm³), a and b (a<b) are the width and length respectively of a rectangular cross-section perpendicular to the applied magnetic field.

2.4.3. Critical temperature (T_c) measurement

Critical temperature measurement was performed by using custom built setup. In this, REBCO sample of size 12 mm × 15 mm was placed between excitation and pick up coil, both of which are made with copper wire with different number of turns. During experiments, an AC voltage is applied to the excitation coil and an AC magnetic field is generated. Induced voltage on the pick up coil is measured using a lock-in amplifier (Signal Recovery 7265). The temperature is measured using a silicon diode temperature sensor (DT-670, Lake Shore Cryotronics, Inc.), which is recorded using a temperature monitoring device (330 temperature controller, Lake Shore Cryotronics, Inc.). During the experiment, a REBCO sample is placed between the excitation and pick up coils and dipped inside a dewar filled with liquid nitrogen to cool the superconductor. After the temperature reaches 77.6 K, the whole assembly of tape sandwiched between two coils is lifted up such that

REBCO is just above liquid nitrogen, and temperature rises slowly. Below T_c , REBCO shields all magnetic field and pick up coil doesn't detect any signal but as soon as REBCO reaches its T_c , a strong signal is detected by the pick up coil. The voltage at the pick up coil vs temperature, provides information about the T_c and ΔT_c of the sample.

2.5. Material characterization of thick REBCO films

Several different material characterization techniques such as General Area Detector Diffraction System (GADDS), Transmission Electron Microscopy (TEM), Inductively Coupled Plasma Mass- Spectrometry (ICP-MS), Profilometer and Focused Ion Beam (FIB) are used to characterize the deposited thick REBCO coated conductors. These techniques are described below.

2.5.1. General Area Detector Diffraction System (GADDS)

X-ray diffraction data for all thick REBCO films presented in this research is obtained using GADDS. The x-ray source used in these measurements was Cu K_α radiation with wavelength ($\lambda = 1.5418 \text{ \AA}$). The X-ray tube was operated at 40 kV and 40 mA. Detector distance was kept constant at 20 cm. For omega-scan, the detector was kept fixed while sample stage was moved continuously from 2° - 34° . Omega scan was used to calculate out-of-plane texture from 005 REBCO peak.

GADDS was also used to obtain in-plane texture of REBCO, which indicates grain-grain misalignment. Pole figure was measured to obtain in-plane texture. For pole figure of 103 REBCO peak, sample stage was kept at $\chi (\chi) \sim 54.74^\circ$, $\omega \sim 16^\circ$ and detector

was kept at $2\theta \sim 32^\circ$. All parameters used for pole figure measurements using GADDS are listed in table 2-2.

Table 2-2. Parameters for pole figure measurements using GADDS.

Number of frames	720
Time/frame	10 sec
Frame width	0.5°
2θ	32°
ω	16°
χ	54.74°
Scan type	Step

The REBCO c -axis lattice parameter was calculated using a least square-fit to the Nelson-Riley function for $(00l)$ peaks of REBCO as given below [105] :

$$F_\theta = \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}, \quad (2-2)$$

where, θ is the location of Bragg peak.

Standard error has been calculated for out-of-plane texture ($\Delta\omega$), in-plane texture ($\Delta\phi$) and c -axis lattice constant. For this, one sample (3.8 μm thick- 15 mol% Zr-doped (Gd, Y)BCO) was selected randomly and used for omega-scan and phi scans for five different times. After each time, the sample was removed from the sample stage, aligned in the z -direction and scanned again. The standard deviation of these five different measurement have been considered as a standard error, which is shown in table 2-3.

Table 2-3. Measured data of in-plane texture, out-of-plane texture and *c*-axis lattice constant (calculated using a least-square fit to Nelson-Riley function) performed on same sample, five different times.

	$\Delta\phi$ (°)	$\Delta\omega$ (°)	REBCO <i>c</i> - lattice constant
1 st measurement	5.5375	1.426	11.756
2 nd measurement	5.7	1.483	11.755
3 rd measurement	5.5855	1.49	11.752
4 th measurement	5.6935	1.487	11.755
5 th measurement	5.7185	1.483	11.754
Standard deviations	0.071911	0.02404496	0.001356

2.5.2. Transmission Electron Microscope (TEM)

Transmission Electron Microscopy (TEM) (JEOL 2000 FX) was used for both cross-section and plan-view analyses of thick REBCO films. Cross-section microstructure was analyzed to check continuity of nanocolumns, appearance of secondary phases, RE₂O₃ precipitates etc. Plan-view was done to calculate the size of nanocolumns and spacing between them. Samples for TEM analysis were prepared by FEI 235 Focused Ion Beam (FIB) milling.

2.5.3. Inductively Coupled Plasma Mass- Spectrometry (ICP-MS) (Agilent Technologies 7700 series)

ICP-MS was used to study the elemental composition of REBCO films with precision at the levels of parts per billion (ppb). Samples size used for the measurement was 3 mm × 12 mm. The concentrations of all the elements (Hf or Zr, Gd, Y, Ba, and Cu) were measured (in ppb quantities), and divided by their atomic weight to get relative concentration. The relative concentration of individual element was divided by the sum of

relative concentrations of all five elements to calculate normalized concentration of each individual element.

2.5.4. Profilometer

Surface step profiler (KLA- Tencor Alpha-Step IQ) was used to measure the thickness of REBCO films. To prepare a step, a part of sample was coated with photoresist material and other part was etched using 10% dilute nitric acid solution. Samples were glued on glass slide using double-sided tape. A scan speed of 20 $\mu\text{m}/\text{sec}$ and scan length of 500-1000 μm were used.

2.5.5. Focused Ion Beam (FIB) (FEI 235)

FIB was used to study the surface features such as a-axis oriented grains , secondary phases present in REBCO. Also, FIB has been used to determine the thickness of some REBCO films.

2.6. Precursor-to-film conversion efficiency calculations.

To calculate precursor to film conversion efficiency (reported in result section - 4), the following calculations has been considered:

Input: (in moles/meter)

$$= [\text{molarity (moles/liter)}] \times [\text{flow(liters/min)}] \times [\text{Deposition time(in min)}] / \text{length}$$

(in m)

Output: (in moles/meter)

Volume of YBCO on actual tape (V_i)

$$= \text{thickness of tape (in m)} \times \text{width of tape (in m)} \times \text{length of tape (in m)}$$

$$= t \times 10^{-6} \times 12 \times 10^{-3} \times 32 \times 10^{-2} \text{ m}^3$$

$$= t \times 384 \times 10^{-11} \text{ m}^3$$

Volume of 1 YBCO unit cell (tetragonal form) (V_2)

$$= (0.386 \times 10^{-9})^2 \times (1.168 \times 10^{-9})$$

$$= 0.17403 \times 10^{-27} \text{ m}^3$$

Number of unit cells on tape (N_u)

$$= V_1/V_2$$

$$= t \times 2206.516 \times 10^{16} \text{ YBCO unit cells}$$

Moles of YBCO on actual tape

$$= N_u / \text{Avogadro number}$$

$$= t \times 2206.516 \times 10^{16} / 6.022 \times 10^{23}$$

$$= t \times 366.406 \times 10^{-7} \text{ moles}$$

Moles of YBCO on actual tape per unit length

$$= \text{moles of YBCO on actual tape} / \text{length of YBCO deposited tape}$$

$$= t \times 366.406 \times 10^{-7} \text{ moles} / 32 \times 10^{-2} \text{ m}$$

$$= t \times 11.450 \times 10^{-5} \text{ moles/m}$$

Moles of cations (Y,Gd,Ba,Cu) on actual tape per unit length:

$$= t \times 11.450 \times 10^{-5} \text{ moles/m} \times 6 \text{ (effective number of cations per YBCO unit cell)}$$

$$= t \times 68.7018 \times 10^{-5} \text{ moles/m}$$

Efficiency (in %):

$$= (\text{output} / \text{input}) \times 100$$

Chapter 3. Results and Discussion.

This section details the finding of this research on fabrication of thick (3.5 μm and above) doped and undoped REBCO using advanced MOCVD. This chapter has been broadly divided into the following categories:

3.1. Thickness dependence study of 5 mol.% Zr-doped (Gd, Y)BCO films up to 4.8 μm thickness.

3.2. Optimizing the composition of thick REBCO [(Gd, Y)BCO] films for high-temperature applications.

3.3. Optimizing composition of thick REBCO ((Gd, Y)BCO) films for low-temperature applications.

3.4. Improving precursor to film conversion efficiency to reduce cost of REBCO films.

3.1. Thickness dependence study of 5 mol.% Zr-doped (Gd, Y)BCO films up to 4.8 μm thickness

Degradation of microstructural quality and critical current density (J_c) with increasing thickness over 2 μm of (Gd, Y)Ba₂Cu₃O_{7-x} ((Gd, Y)BCO) film has been an obstacle in further improving its current carrying capability. In this section, the microstructural and electromagnetic properties of 5 mol.% Zr-doped (Gd, Y)BCO films with thicknesses ranging from 1.1 to 4.8 μm have been investigated. These films were deposited on a Hastelloy/Al₂O₃/MgO/LaMnO₃ substrate in a single pass using Advanced Metal Organic Chemical Vapor Deposition (A-MOCVD).

3.1.1. Effect of thickness on critical current density (J_c) at 77 K, 0 T

Figure 3-1 shows the critical current density (J_c) thickness dependence of 5 mol.% Zr-doped (Gd, Y)BCO films at 77 K, 0 T. Thirteen films with various thickness, between 1.1 and 4.8 μm , showing similar critical current densities of between 1.3 and 2 MA/cm² are shown in the figure 3-1. There is not a sharp decrease in self field J_c with increasing thickness, as had been shown by some research groups, which suggests that there is no formation of any sort of dead layer [33,65,94,95]. All of the tested films show a similar self-field J_c , but the actual value is little lower than that of undoped films, as these are all doped (Gd, Y)BCO films, intended to form continuous BaZrO₃ nanorods to improve in-field performance. BaZrO₃ nanocolumns, due to high lattice mismatch with (Gd, Y)BCO, induces positive strain in the film. This increases the *c*-lattice constant of the (Gd, Y)BCO matrix, degrading crystallinity and texture of the film leading to the deterioration of self field J_c [81,106]. Nevertheless, we have achieved high self-field J_c of 3.3 MA/cm² in 4+

μm thick undoped (Gd, Y)BCO films, as shown in figure 3-2 [107]. All samples show critical current of over 1400 A/12 mm and critical current density above 2.6 MA/cm². The highest critical current at 77 K, 0 T achieved is over 1660 A/12 mm in a 4.6 μm thick (Gd,Y)BCO film, which is very much comparable to the highest ever critical current of 1500 A/cm-width, reported in a 5 μm thick SmBCO film, both with a same J_c of 3 MA/cm² [93].

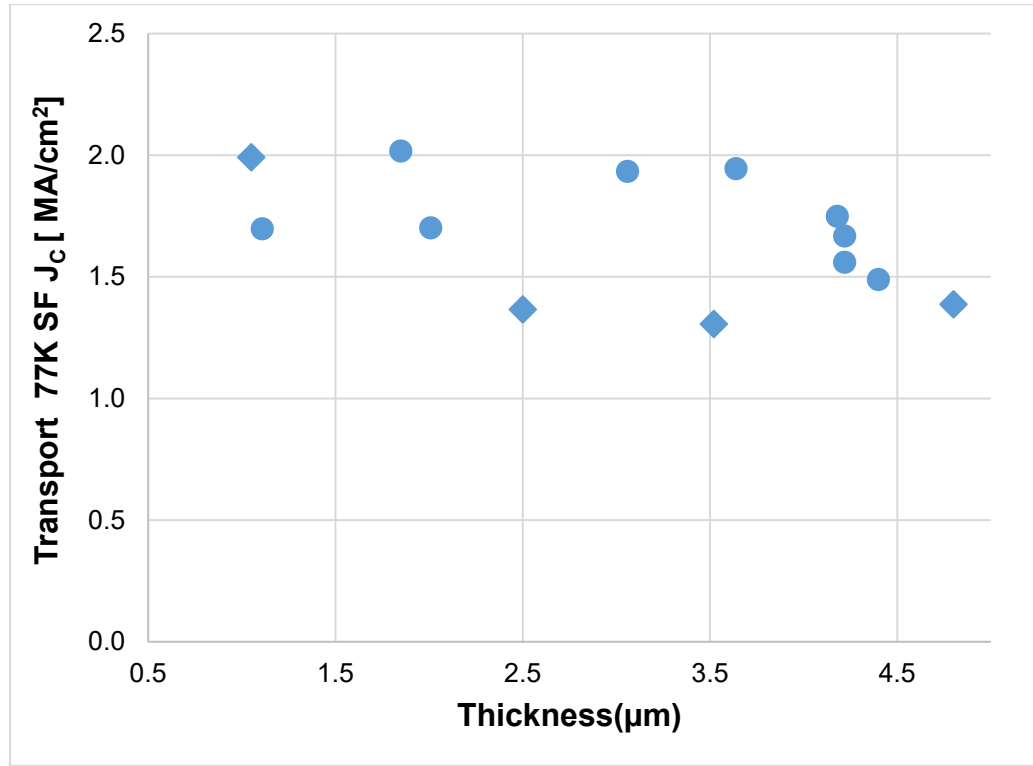


Figure 3-1. Transport critical current density (J_c) dependence on thickness at 77 K, 0 T for 5 mol.% Zr-doped (Gd, Y)BCO films.

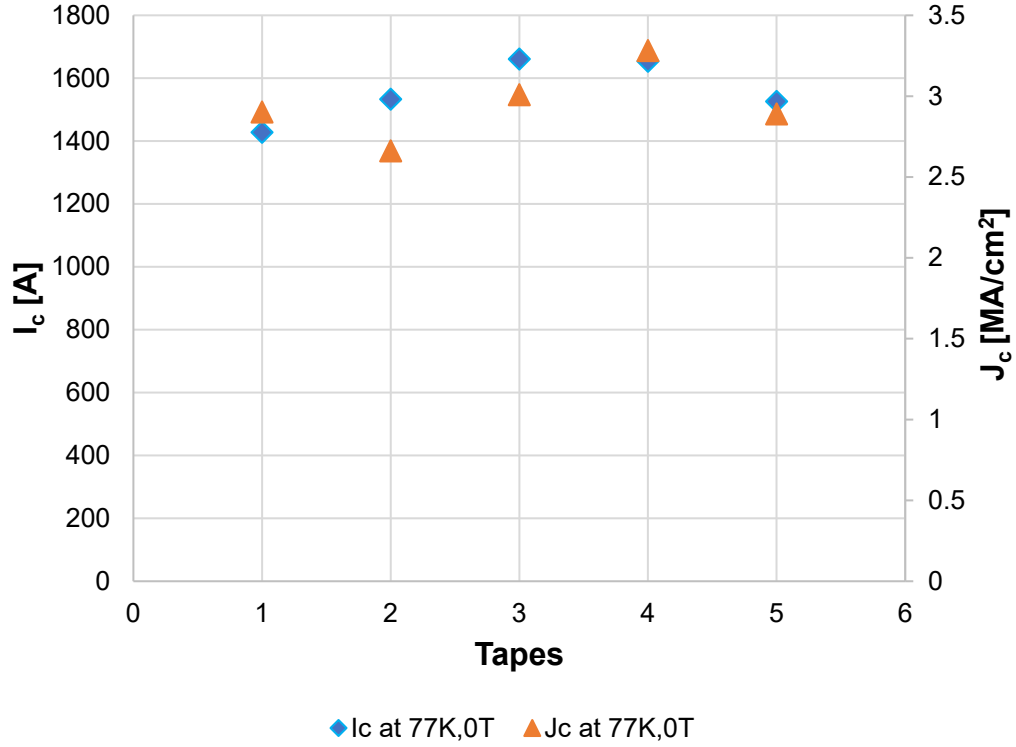


Figure 3-2. Transport critical current (I_c) and critical current density (J_c) of five different 4+ μm thick undoped (Gd, Y)BCO films at 77 K, 0 T.

3.1.2. Effect of thickness on texture and superconducting critical temperature

Figure 3-3 depicts in-plane texture and out-of-plane texture of eleven different 5 mol.% Zr-doped (Gd, Y)BCO tapes having a thickness ranging from 1.1 to 4.8 μm . The in-plane texture has been investigated by XRD ϕ -scan of (Gd, Y)BCO (103) peak. The full-width-at-half-maximum values of (Gd, Y)BCO (103) peak for 11 different samples are in the range of 2.5–3.5°. Such a consistent in-plane texture indicates that there is no loss of crystallinity and no coarsening of grains with increasing film thickness [65]. Also, no change in grain sizes and grain boundaries with increasing thickness indicates a good control of surface roughness, which is essential to avoid any formation of misoriented a-axis grains [65]. The out-of-plane texture has been calculated by XRD ω -scan of (Gd,

Y)BCO (005) peak. All full-width-at-half-maximum values of (Gd, Y)BCO (005) peak for 11 different samples are in the range of 0.9–1.5°. Such a consistent and sharp in-plane and out-of-plane texture of films with thickness ranging from 1.1 to 4.8 μm prove that with better process control of A-MOCVD, a homogeneous and high-quality microstructure can be achieved for any film thickness. Also such consistent and good in-plane and out-of-plane texture validate the consistency in self field J_c as shown in figure 3-1.

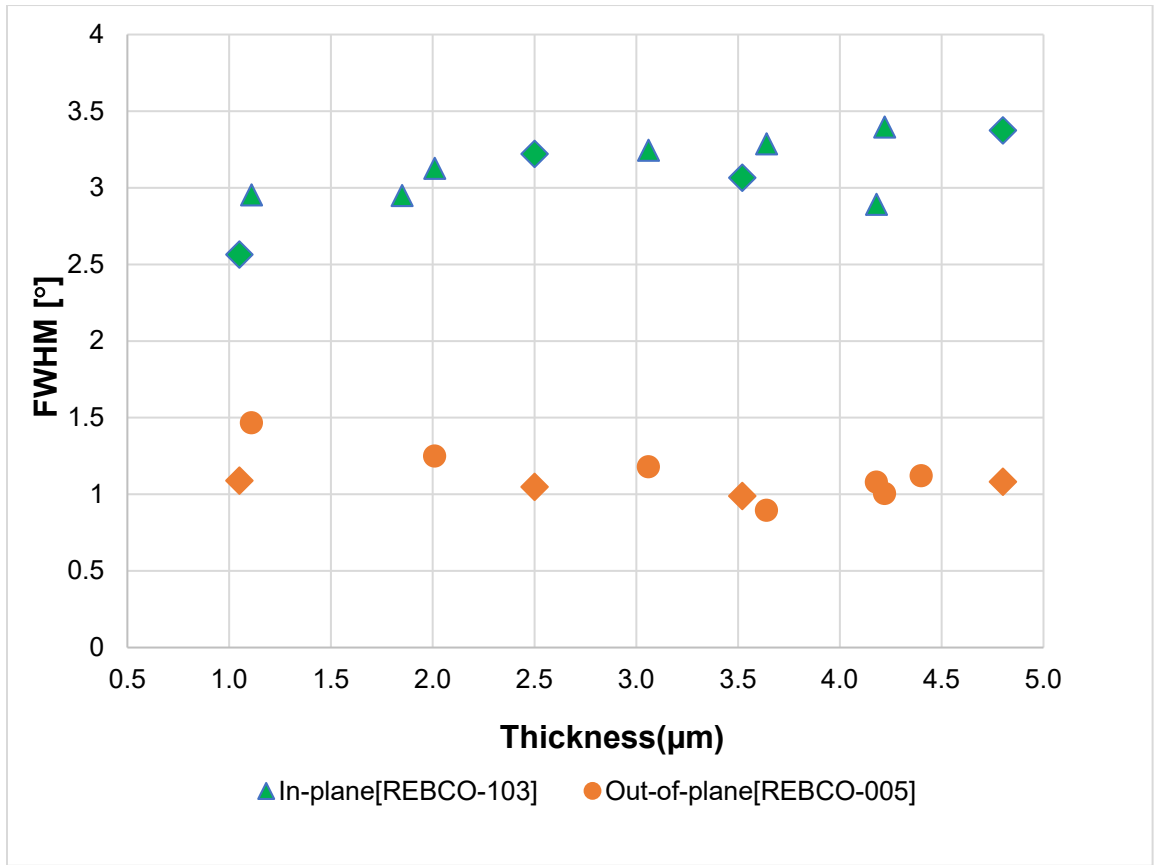


Figure 3-3. Thickness dependence of out-of-plane texture and in-plane texture (shown in degrees (FWHM)) from (Gd, Y)BCO(005) ω -scans and (Gd, Y)BCO(103) ϕ -scans, respectively, of 5 mol.% Zr-doped (Gd, Y)BCO films).

Figure 3-4 presents the onset critical transition temperature ($T_{c, \text{onset}}$) and the transition width (ΔT_c) of eleven different 5 mol.% Zr-doped (Gd, Y)BCO tapes with thickness varying from 1.1 to 4.8 μm . The onset critical transition temperature ($T_{c, \text{onset}}$)

was determined as 90% of the maximum induced voltage of the pick-up coil and the transition width (ΔT_c) = $T_{c, 90\%} - T_{c, 10\%}$ after normalizing the pick-up voltage of the coil. $T_{c, onset}$ of all eleven different tapes with thickness up to 4.8 μm are in a good range of 90.2–91.7 K and ΔT_c is in the range of 0.4–1.1 K. This result is in contrast with published works by some research groups showing a decrease of $T_{c, onset}$ and increase in ΔT_c with increase in film thickness [94,98]. Such high $T_{c, onset}$ with narrow ΔT_c suggests the absence of any secondary phases and also reflects the homogeneous nature of these films. Also, no degradation in the high onset critical transition temperature ($T_{c, onset}$) with increasing thickness indicates that there are no extra strains induced in the (Gd, Y)BCO matrix which can alter the carrier density in the superconductor and can lower $T_{c, onset}$. This result of high and consistent $T_{c, onset}$ and sharp ΔT_c agrees well with the consistency in self field J_c shown in figure 3-1 and good and constant texture shown in figure 3-3.

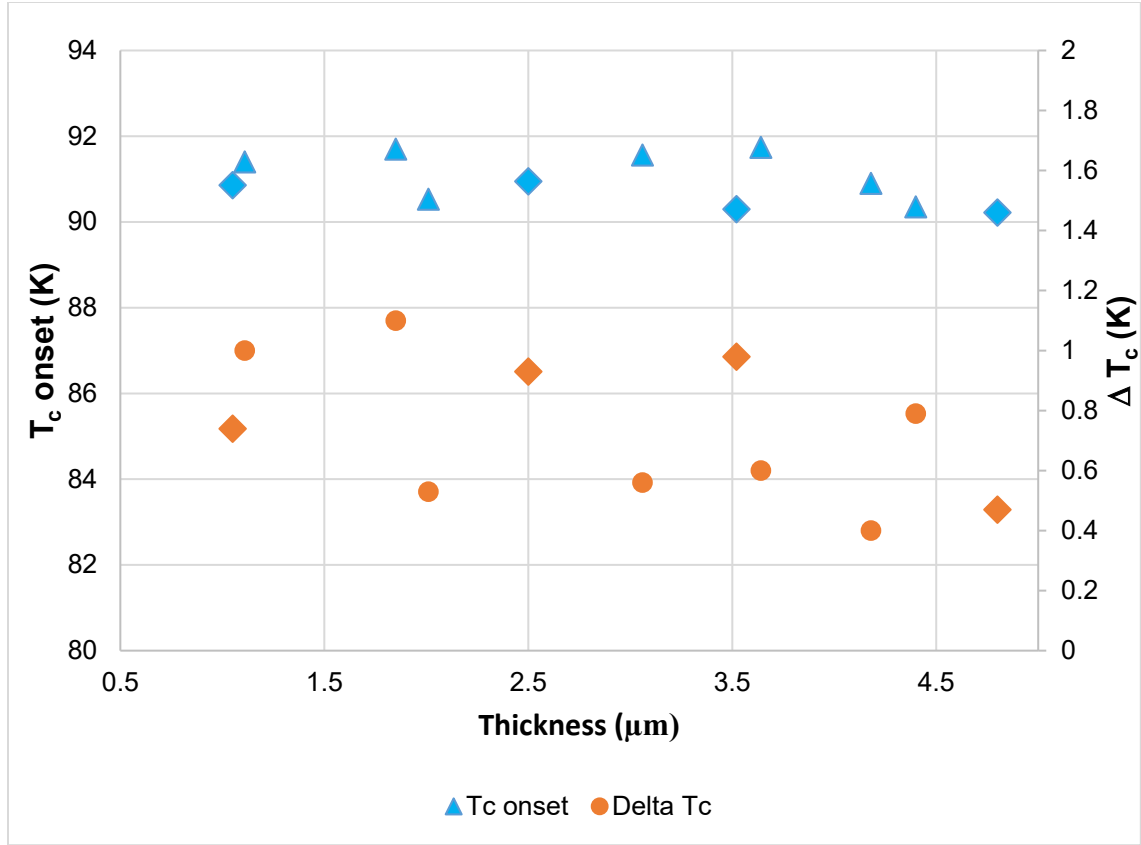


Figure 3-4. Thickness dependence of superconducting onset critical transition temperature (T_c) and transition width (ΔT_c) of 5 mol% Zr-doped (Gd, Y)BCO films.

3.1.3. Effect of film thickness on in-field critical current density

Figure 3-5 demonstrates the critical current density of 5 mol% Zr-doped (Gd, Y)BCO tapes with thicknesses of 1.1, 2.5, 3.5, and 4.8 μm at 65 K in magnetic field up to 9 T, applied parallel to the c -axis direction of (Gd, Y)BCO. These four films have been indicated in Figures 3-1, 3-3 and 3-4 with diamond shapes. Above 4 T, the J_c values are very close for all samples with different thicknesses, while below 4 T, the 4.8 μm film tends to dominate until 0.4 T, with a J_c of 3 MA/cm² at 1.5 T, which corresponds to a very high critical current of 1734 A/12 mm. Other films with thicknesses of 1.1, 2.5, and 3.5 μm show very close J_c values of 2.7 MA/cm², 2.6 MA/cm², and 2.8 MA/cm² at 1.5 T,

corresponding to a critical current of 352 A/12 mm, 775 A/12 mm and 1167 A/12 mm respectively. However, at 65 K, 0 T, the 1.1 μm sample shows a higher critical current density of 4.5 MA/cm², while other tapes show slightly lower self-field J_c values of ~ 3.2 MA/cm². It can also be validated from self field J_c at 77 K shown in figure 3-1, where this particular 1.1 μm film (denoted by diamond shape) shows a higher self field J_c of 2 MA/cm² while other films of 2.5, 3.5, and 4.8 μm thick films (denoted by diamond shape) show lower but consistent self field J_c of ~ 1.4 MA/cm². Also, the 4.8 μm film shows a distinctive plateau behavior of between 0.2 and 3 T, indicating slower decay of J_c with increasing field, and hence relatively higher retention of J_c in that range. This plateau at 65 K, lower fields, seems to appear in all films but becomes more prominent with an increase in thickness. The plateau feature had been shown by few research groups [108,109], at high temperature and below the matching field. It was shown that below the matching field, J_c is independent of the applied magnetic field ($B \parallel c\text{-axis}$) which can be possible in the single vortex pinning regime, if all the nanocolumnar defects are continuous and provide identical pinning, reducing vortex mobility with perfect occupancy of columnar defects. It had been suggested that pinning efficiency is mainly reduced by thermal fluctuations which reduces the binding energy of vortex in the pinning potential well [109,110]. In addition, it had been suggested that thermal processes in vortex depinning of isotropic defects is $1/\varepsilon$ ($1/\varepsilon$ length of nanocolumnar defects) times higher than that of columnar defects, indicating the effect of nanocolumnar length. With increasing thickness, continuous nanocolumn length will increase which will be less susceptible thermal fluctuations and contribute to better pinning. Although, at this point, there is no analytical study available to prove the effect of thickness on this plateau behavior, it is proposed that film thickness seems to effect the

pinning in $B \parallel c$ -axis direction probably due to confining large section of the vortex length. It is important to note here that all the differences appear before 4 T, which seems to have some significance as will be explained later.

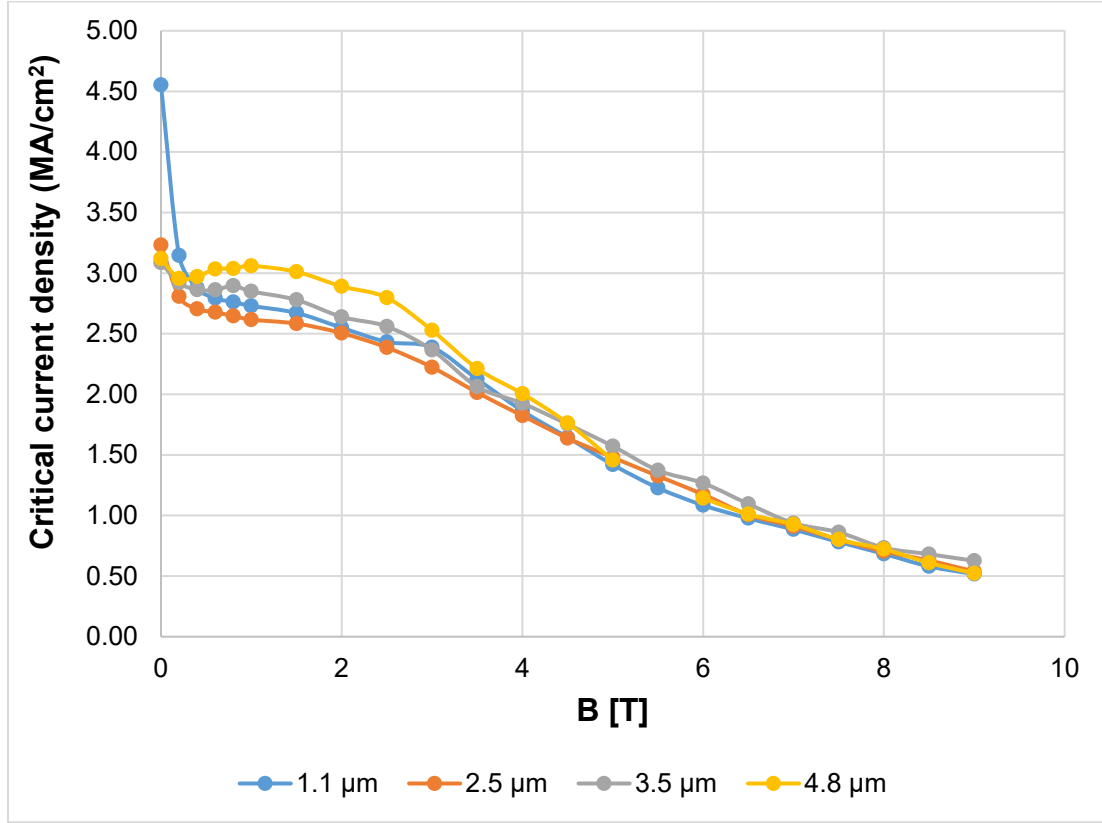


Figure 3-5. Critical current density (J_c) of 5 mol% Zr-doped (Gd, Y)BCO films with a thickness of 1.1, 2.5, 3.5, and 4.8 μm at 65 K in a magnetic field up to 9 T applied along the c -axis.

Figure 3-6 shows the pinning force (F_p) = $J_c \times B$ versus magnetic field up to 9 T, applied perpendicular to c -axis for 5 mol% Zr-doped (Gd, Y)BCO tapes with film thicknesses of 1.1, 2.5, 3.5, and 4.8 μm at 65 K. The 4.8 μm sample performs better in high temperature and shows a higher peak pinning force (F_p) of 87 GN/m^3 , while the 1.1, 2.5, and 3.5 μm samples show peak pinning force values of 75 GN/m^3 , 74 GN/m^3 , and 79 GN/m^3 respectively. The higher peak pinning force in the 4.8 μm results in the higher J_c

value of this film as shown in Figure 3-5. Matching field denotes the field at which the density of vortices equals the density of correlated defects. The approximate matching field (B_ϕ) can be estimated from the position of the peak on a plot of pinning force vs magnetic field, which relates very well with matching field calculated from nanorods spacing [111]. According to this calculation, matching field values of 4, 5, 4.5 and 4 T respectively were determined for the 1.1, 2.5, 3.5, and 4.8 μm films. At 65 K, as shown in [111], in-field pinning mechanism is mostly governed by BaZrO_3 nanocolumns. Consistency in the matching field (calculated from pinning force plot in Figure 3-6) indicates a similar density of nanorods in all films independent of the thickness.

At this point, it is important to revisit Figure 3-5. The magnetic field at which the J_c of all films with different thickness merges is $\sim 4\text{-}5$ T which is similar to the value estimated to be the matching field of these films. Thus these films show similar results in the collective pinning regime (after the matching field) but slight differences before the matching field. After reaching the matching field, the number of vortices exceeds the number of nanocolumnar defects and the interactions between vortices increases, leading to rapid depinning of vortices which then get pinned collectively by different defects.

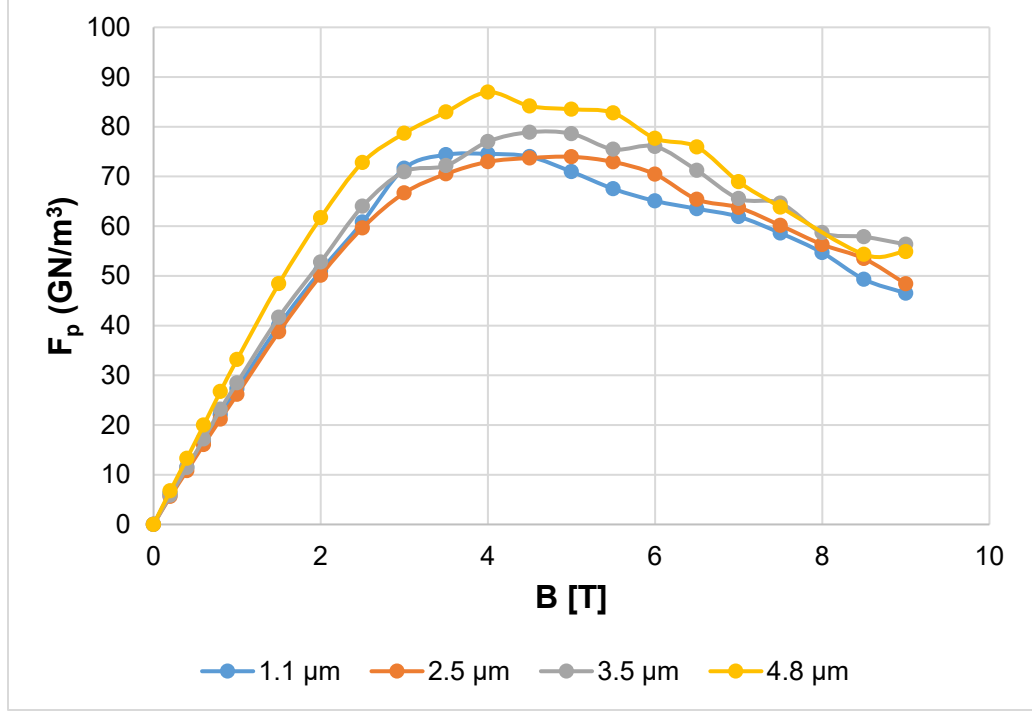


Figure 3-6. Pinning force (F_p) of 5 mol% Zr-doped (Gd, Y)BCO films with thicknesses of 1.1, 2.5, 3.5, and 4.8 μm at 65 K ($B \parallel c$) in magnetic fields up to 9 T.

Figure 3-7 illustrates the critical current density (J_c) angular dependence, ranging from -93° to 30° , of 5 mol.% Zr-doped (Gd, Y)BCO tapes with thicknesses 1.1, 2.5, 3.5, and 4.8 μm at 30 K, 3 T. All four films with various thicknesses show peaks in the orientation of magnetic field perpendicular to c -axis ($B \perp c$) and magnetic field parallel to c -axis ($B \parallel c$ -axis). These peaks should be due to enhanced pinning in these orientations by in-plane precipitates along the ab -direction and continuous nanorods along the c -axis direction respectively. J_c at $B \parallel c$ -axis varies within a narrow range of 10–11 MA/cm^2 , which indicates the similar pinning characteristics by the nanorods of similar density, independent of film thickness. The 1.1 μm sample shows a J_c of 11 MA/cm^2 at $B \parallel c$, which corresponds to a critical current of 1435 A/12mm, while the 4.8 μm thick film shows

a very similar J_c of 10.3 MA/cm², corresponding to a critical current of 5938 A/12mm. Films with 2.5 and 3.5 μm also show a very similar J_c of 10.3 MA/cm², corresponding to a critical current of 3096 A/12mm and 4316 A/12mm respectively. However, J_c at $B \perp c$ is found to show some differences in films of different thicknesses. J_c at $B \perp c$ for 1.1 μm is 16.7 MA/cm², while for the 4.8 μm film, this value is 14.2 MA/cm². Films with thicknesses of 2.5 and 3.5 μm show J_c of 14 MA/cm² and 13 MA/cm² at $B \perp c$ -axis respectively. The J_c values at the $B \perp c$ -axis for 2.5, 3.5, and 4.8 μm thick films are very close, but for the 1.1 μm thick film, the critical current density is higher, which could be due to a greater density of in-plane defects such as RE₂O₃ precipitates in the thinner film. RE₂O₃ precipitates have lower in-plane lattice mismatch with (Gd, Y)BCO and can readily nucleate at the surface of growing (Gd, Y)BCO films. These RE₂O₃ precipitates grow in particles or plates form, mostly in ab plane of (Gd, Y)BCO, that tends to improve self field J_c and pinning properties [87,92,112–114]. At all angle orientations other than $B \perp c$ -axis, all films show similar critical current density with variation in the range of less than 1 MA/cm².

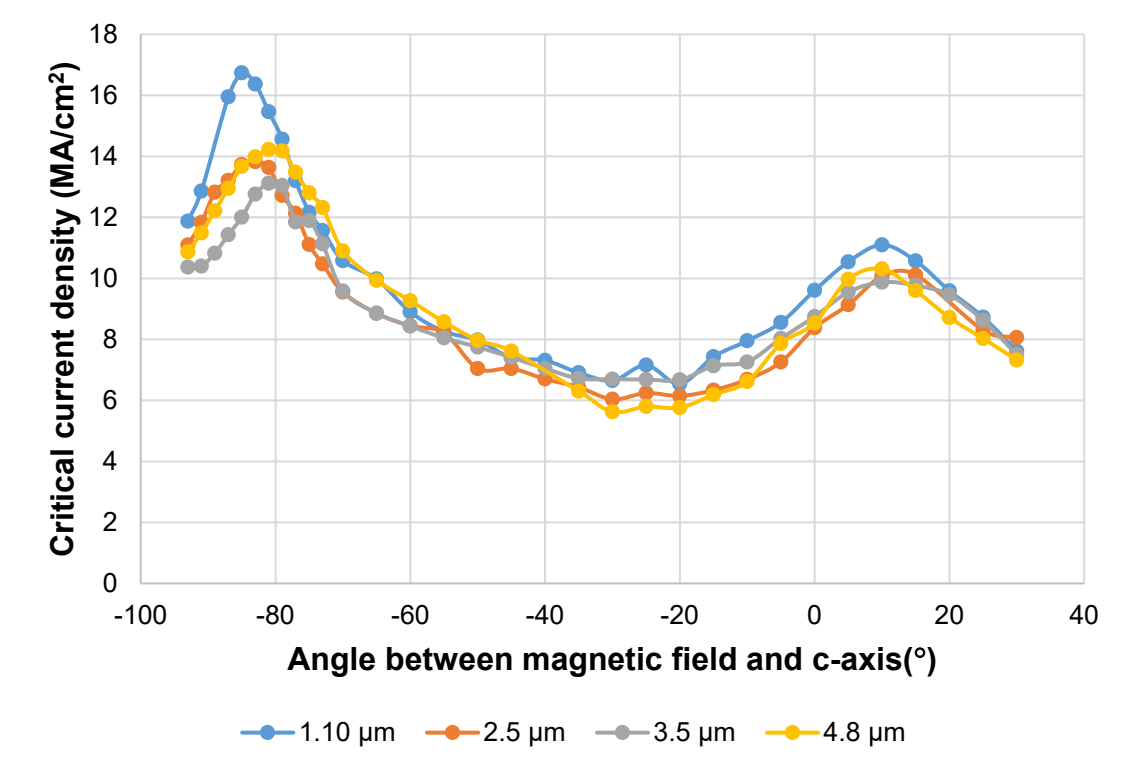


Figure 3-7. Angular dependence of critical current density (J_c) of 5 mol.% Zr-doped (Gd, Y)BCO films with thicknesses of 1.1, 2.5, 3.5, and 4.8 μm at 30 K in 3 T magnetic field.

Figure 3-8 shows the critical current density at 30 K in magnetic field up to 9 T applied along the c -axis for 5 mol% Zr-doped (Gd, Y)BCO tapes of thicknesses 1.1, 2.5, 3.5, and 4.8 μm . Above 4 T, the characteristics of all tapes with different film thickness merge and show very similar J_c values, while below 4 T (approximate matching field from Figure 3-6), some difference is observed. The 1.1 μm film shows a higher self-field J_c at 30 K, following the same trend as was shown in Figure 3-1 with higher self-field J_c at 77 K, probably due to higher density of RE_2O_3 precipitates. The self-field J_c values at 30 K for 2.5, 3.5, and 4.8 μm films are 19, 17, and 19 MA/cm^2 , respectively.

From 0.2 – 2 T, the J_c increases from 3.5 μm to 2.5 μm and then to 4.8 μm and 1.1 μm . It is interesting to see that J_c below matching field ($\sim 4\text{-}5$ T) at 30 K ($B \parallel c\text{-axis}$) is not following the same trend at 65 K as shown in Figure 3-5. This indicates some different pinning mechanism occurring below matching field at 30 K. It has been well documented that below matching field, pinning along $B \parallel c\text{-axis}$ is dominated by continuous columnar defects [108,109]. Also, with reducing temperature, vortex core size gets reduced from $\sim (5.7\text{-}7.6)$ nm at 65 K to $(3.6\text{-}4.9)$ nm at 30 K, that can give rise to some different pinning mechanism. Although, at this point it is difficult to make any claims on the difference of J_c showed by the films at low fields and more in-depth study of the microstructure and the interface between nanorods and (Gd, Y)BCO matrix needs to be done to understand the reason of this variation, which is out of the scope of this thesis.

The J_c values of all 5 mol.% Zr-doped (Gd, Y)BCO films with thicknesses 1.1, 2.5, 3.5, and 4.8 μm merge around 4-5 T, which is the estimated matching field from Figure 3-6. After the matching field, vortex-vortex interaction becomes stronger, leading to the mobility of vortices, which gets collectively pinned by different defects. The similar J_c beyond the matching field indicates similar collective pinning in all films independent of thickness. As a result at 30 K, 9 T ($B \parallel c$), all films with thicknesses of 1.1, 2.5, 3.5, and 4.8 μm show a similar J_c of ~ 3.8 MA/cm².

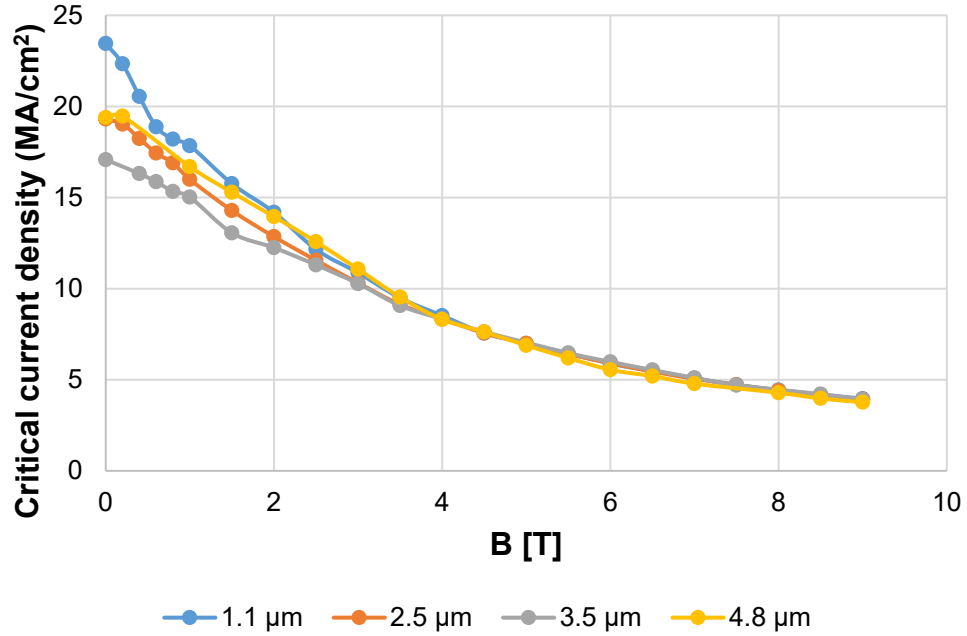


Figure 3-8. Critical current density (J_c) of 5 mol% Zr-doped (Gd, Y)BCO films with thicknesses of 1.1, 2.5, 3.5, and 4.8 μm at 30 K in magnetic fields of up to 9 T applied along the c -axis.

3.1.4. Effect of thickness on (Gd, Y)BCO c -axis lattice constant

Table 3-1 reports the c -axis lattice constant of (Gd, Y)BCO determined from the (00 l) peaks by a least-squares fit to the Nelson-Riley function [105]. All 5 mol.% Zr-doped (Gd, Y)BCO tapes with thicknesses of 1.1, 2.5, 3.5, and 4.8 μm show a very close c -lattice constant, in the range of 11.734–11.742°. This consistent c -axis lattice of (Gd, Y)BCO for films of various thicknesses removes the possibility of any compositional variations or any hindrance due to inadequate oxygenation of the thicker films. Also, consistent c -lattice constant indicates similar strain caused in the (Gd, Y)BCO film with similar density of BaZrO₃ nanocolumns, independent of thickness. This relates well with consistency shown in self field J_c at 77 K (figure 3-1), texture (figure 3-3), critical transition temperature

(figure 3-4). Also, the matching field calculated using figure 3-6 indicates a similar density of nanocolumns which relates well with the consistency in *c*-lattice constant.

Table 3-1. *c*-lattice parameter of (Gd, Y) BCO calculated from XRD scans. These values were generated using the Nelson-Riley function of all (00*l*) peaks of 5 mol% Zr-doped (Gd, Y)BCO films with a thickness of 1.1, 2.5, 3.5, and 4.8 μm .

Thickness [μm]	1.1	2.5	3.5	4.8
<i>c</i> -lattice constant ((Gd,Y)BCO) [$\text{\AA}$]	11.735	11.734	11.742	11.734

3.1.5. Summary

An advanced MOCVD (A-MOCVD) reactor has been used to deposit 5 mol.% Zr-doped (Gd, Y)BCO films in single-pass depositions, with film thicknesses ranging from 1.1 to 4.8 μm . A consistent J_c independent of thickness has been attained in the range of 1.3–2.0 MA/cm² at 77 K, 0 T. Excellent in-plane texture below 3.5° and out-of-plane texture below 1.5° with high onset critical temperature ($T_{c,\text{onset}}$) in the range of 90.2–91.7 K and transition width (ΔT_c) below 1.1 K have been shown for eleven different films of 5 mol.% Zr-doped (Gd, Y)BCO tapes with thicknesses of 1.1 to 4.8 μm . At high temperature (e.g., 65 K) in a magnetic field of up to 9 T ($B \parallel c$), similar performance has been achieved for 5 mol% Zr-doped (Gd, Y)BCO tapes with thickness varying from 1.1 to 4.8 μm . A very high J_c of 3 MA/cm² and pinning force (F_p) of 87 GN/m³ have been shown for 4.8 μm thick 5 mol% Zr-doped (Gd, Y)BCO tapes at 65 K, 1.5 T ($B \parallel c$), which exceeds the performance of its 1.1 μm counterpart. Also at 30 K, 3 T, angular dependence of critical current four different 5 mol% Zr-doped (Gd, Y)BCO films with thicknesses of 1.1, 2.5, 3.5, and 4.8 μm films showed no sign of any degradation with increasing thickness at any orientation, an a high and consistent J_c value of ~ 10 MA/cm² at 30 K, 3 T ($B \parallel c$).

3.2. Optimizing the composition of thick REBCO [(Gd, Y)BCO] films for high-temperature applications

(Gd, Y)BCO [or REBCO] can be used for various high-temperature electric-power applications, such as underground transmission cables, fault current limiters, transformers at 65-77 K in the magnetic field of 0–0.5 T, and for large-scale motors and generators at 65 K in the magnetic field of 1-5 T [115]. High-temperature applications are cost-effective as they use less complicated cryogenic systems and inexpensive cryogens (e.g., liquid nitrogen) compared to the costly and complicated cryogenic systems required for low-temperature applications with expensive cryogens (e.g., liquid helium).

This section has been divided into the following sub-sections each detailing optimization of the composition of REBCO for high-temperature applications.

3.2.1 Optimizing dopant concentrations to achieve 1440 A/cm at 65 K, 1.5 T ($B \parallel c$ -axis).

3.2.2. Improving the isotropic pinning properties of 5 mol%-doped (Gd, Y)BCO films at 65 K in magnetic fields of 1.5 T and 0.25

3.2.2.1. The effect of molarity on the microstructural and transport properties of 5 mol% zirconium (Zr)-doped (Gd, Y)BCO film.

3.2.2.2. The effect of different dopant, hafnium (Hf), at low concentrations (5 mol%).

3.2.2.3. The effect of RE₂O₃ on the microstructural and transport properties of 5 mol% Zr-doped (Gd, Y)BCO and 5 mol% Hf-doped (Gd, Y)BCO.

3.2.1 Optimizing dopant concentration to achieve 1440 A/cm at 65 K, 1.5 T (B || *c*-axis)

It is well established that *c*-axis-aligned, self-assembled, non-superconducting continuous nanocolumnar defects, such as BaZrO₃ (BZO), provide strongly correlated pinning at the B || *c*-axis of (Gd, Y)BCO [36,46,73]. Some groups have systematically studied dopant concentration and its effect at high temperatures (77 – 65 K) and different magnetic fields for samples with thicknesses under 2 μm [48,81,83,85,116]. However, there are only limited studies on the effect of dopant concentration in films thicker than 2.5 μm [49,94,95]. The performance of these films has not been noteworthy due to an observed drop in J_c with increasing thickness [49,94,95]. Due to the limitation of growing films above 2 μm, it is very difficult to further increase the critical current and reach the very high value of 1440 A/cm at 65 K, 1.5 T (B || *c*-axis). However, as mentioned in Section 3.1, it has been demonstrated that thick films over 4 μm can be grown without considerable degradation in self-field or in-field J_c using an A-MOCVD reactor. The purpose of this study is to determine the dopant concentration in thick (Gd, Y)BCO films best suited for high-temperature applications in a magnetic field.

3.2.1.1. The effect of dopant concentration on self-field J_c at 77 K

Transport self-field J_c at 77 K decreases sharply with increasing dopant concentration, as shown in Figure 3-9. Undoped (Gd, Y)BCO films with thicknesses ranging from 3.8 to 4.8 μm show a high self-field J_c of 2.2 to 3.2 MA/cm² at 77 K. Increasing dopant (Zr = zirconium) concentration to 5 mol%, the 77 K self-field J_c of these 3.5 to 4.8 μm films reduces to 1.2 to 1.3 MA/cm². Further increasing the dopant (Zr)

concentration to 15 mol%, the 77 K self-field J_c decreases to the much lower range of 0.63 to 0.68 MA/cm² with films ranging in thickness from 3.5 to 4.8 μ m. This decrease in 77 K self-field J_c is due to the increase in the density of non-superconducting nanocolumnar defects (e.g., BaZrO₃) grown to increase the in-field properties. The higher density of nanocolumnar defects induces more microstrains in the films that contribute to a degradation in texture and self-field properties [81,83,106].

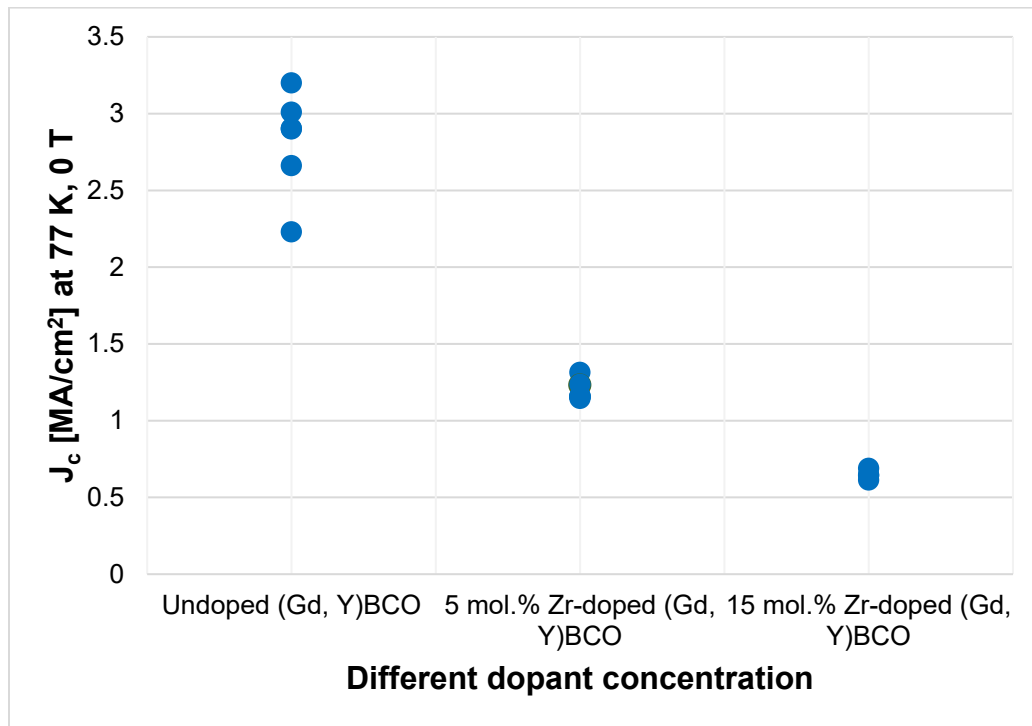


Figure 3-9. Transport critical current density (J_c) at 77 K, 0 T for undoped and Zr-doped (5 and 15 mol%) (Gd, Y)BCO films that are 3.5 – 4.8 μ m thick.

3.2.1.2. The effect of dopant concentration on texture

Table 3-2 shows the results of out-of-plane texture, in-plane texture, c -axis lattice constant and (Ba-Zr)/Cu ratio of an undoped (Gd, Y)BCO, a 5 mol% Zr-doped (Gd, Y)BCO, and a 15 mol% Zr-doped (Gd, Y)BCO film. The out-of-plane texture was calculated by XRD ω -scan of (Gd, Y)BCO (005) peak. Full-width-at-half-maximum values

of the (Gd, Y)BCO (005) peak increase with increasing dopant concentration from 0.94° for undoped (Gd, Y)BCO to 1.08° for 5 mol% Zr-doped (Gd, Y)BCO, and further to 1.36° for 15 mol% Zr-doped (Gd, Y)BCO. The in-plane texture was investigated by XRD ϕ -scan of the (Gd, Y)BCO (103) peak. The full-width-at-half-maximum values of the (Gd, Y)BCO (103) peaks follow the same trend as the out-of-plane texture, also increasing with increasing dopant concentrations. It increases from a very sharp in-plane texture of 2.33° for undoped (Gd, Y)BCO to 3.38° for 5 mol% Zr-doped (Gd, Y)BCO to a high 5.54° for 15 mol% Zr-doped (Gd, Y)BCO. This texture worsening is likely the effect of microstrains caused by the increased density of the nanorods, which disturbs the crystallinity of the film. The c -axis lattice constant of (Gd, Y)BCO was determined from the (00 l) peaks by a least-squares fit to the Nelson-Riley function [105]. It increases from $11.68 \text{ \AA}$ for undoped (Gd, Y)BCO to $11.73 \text{ \AA}$ for 5 mol% Zr-doped (Gd, Y)BCO and further to $11.75 \text{ \AA}$ for 15 mol% Zr-doped (Gd, Y)BCO. As reported by Cantoni et al., the increase in BZO nanocolumn concentration results in a positive strain in the (Gd, Y)BCO matrix along the c -axis, leading to an increase in (Gd, Y)BCO c -lattice parameters [106]. (Ba-Zr)/Cu indicates the residual barium (Ba) in the matrix after removing Zr from the total Ba measured by ICP-MS. This seems more appropriate when comparing different dopant concentrations with undoped (Gd, Y)BCO. (Ba-Zr)/Cu remains almost constant from undoped (Gd, Y)BCO to 5 mol% Zr-doped (Gd, Y)BCO indicating an increase in the c -lattice parameter of REBCO is not the effect of Ba in the matrix due to Ba-rare earth cation substitution. It seems to be an effect of the formation of nanorods and their interaction with the (Gd, Y)BCO matrix. Although, for 15 mol% Zr-doped (Gd, Y)BCO films, (Ba-Zr)/Cu seems to be higher, which is due to excessive Ba in the overall composition. The effect of Ba with constant dopant

concentration will be discussed in a later section of the results. The increase in the c -lattice constant of (Gd, Y)BCO contributes to the decreased self-field J_c , as shown in Figure 3-9, as the distance between the highly conductive Cu-O planes increases, reducing the charge concentrations. Also, the increase in strain in the (Gd, Y)BCO matrix caused by increases in the c -lattice constant of (Gd, Y)BCO can deteriorate the texture, as shown in Table 3-2.

Table 3-2. Out-of-plane texture and in-plane texture from (Gd, Y)BCO(005) ω -scans and (Gd, Y)BCO(103) ϕ -scans respectively of an undoped (Gd, Y)BCO film, and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO film.

	Out-of-plane texture (°)	In-plane texture (°)	(Gd, Y)BCO c -lattice constant	(Ba-Zr)/Cu
Undoped (Gd, Y)BCO	0.94	2.33	11.68	0.65
5 mol% Zr-doped (Gd, Y)BCO	1.08	3.38	11.73	0.66
15 mol% Zr-doped (Gd, Y)BCO	1.36	5.54	11.75	0.70

3.2.1.3. The effect of dopant concentration on in-field critical current at 65 K

Figure 3-10 shows the transport critical current density of undoped (Gd, Y)BCO, 5 mol% Zr-doped (Gd, Y)BCO, and 15 mol% Zr-doped (Gd, Y)BCO films with thicknesses of 3.8 μm , 4.8 μm , and 3.8 μm respectively at 65 K in a magnetic field of 0 to 9 T applied parallel to the c -axis of (Gd, Y)BCO. Self-field J_c at 65 K follows the same trend as the self-field J_c at 77 K. Undoped (Gd, Y)BCO film shows the highest self-field J_c of $\sim 4.1 \text{ MA/cm}^2$ at 65 K while the 5 mol% Zr-doped film has a lower self-field J_c of $\sim 3.1 \text{ MA/cm}^2$, followed by the 15 mol% Zr-doped film with a J_c of 1.5 MA/cm^2 . However, as the magnetic field is applied, a sharp drop in the J_c of undoped (Gd, Y)BCO is observed compared with the doped (Gd, Y)BCO due to the absence of any nanocolumnar defects to pin the vortices. When the magnetic field is applied, vortices (or flux lines) start penetrating the film. In the presence of an electric current, a Lorentz force acts on the vortices, resulting in vortex

motion, which causes the dissipation of energy and electrical resistance appears in the superconductor. Only when the vortices can be pinned by a counteracting pinning force, can a superconductor achieve a high J_c . As the field is applied parallel to the c -axis of (Gd, Y)BCO, nanocolumnar defects (BaZrO_3) aligned parallel to the c -axis of (Gd, Y)BCO effectively immobilize the vortices and increase the in-field J_c . As a result, at a magnetic field of 1.5 T applied parallel to the c -axis of (Gd, Y)BCO, undoped (Gd, Y)BCO shows a lower J_c of $\sim 1 \text{ MA/cm}^2$, while 5 mol% Zr-doped (Gd, Y)BCO has a three-fold higher J_c of 3 MA/cm^2 and 15 mol% Zr-doped (Gd, Y)BCO $\sim 50\%$ higher J_c of 1.5 MA/cm^2 . It is also important to note that the 3 MA/cm^2 of 5 mol% Zr-doped (Gd, Y)BCO at 65 K, 1.5 T ($B \parallel c$ -axis) generates a record value of 1445 A/cm, which meets our project goal of 1440 A/cm. The retention factor at 65 K, 1.5 T ($B \parallel c$ -axis) [defined as the ratio of I_c at 65 K, 1.5 T ($B \parallel c$ -axis) to I_c at 65 K, 0 T] for 5 mol% (Gd, Y)BCO and 15 mol% (Gd, Y)BCO are 0.96 and 0.99 respectively and much higher than the retention factor of 0.25 for undoped (Gd, Y)BCO. The reason underlying the lower J_c value of 15 mol% Zr-doped (Gd, Y)BCO, compared with 5 mol% (Gd, Y)BCO, is the detrimental effect of the lower self-field J_c of 15 mol% Zr-doped (Gd, Y)BCO due to the higher density of nanorods.

As the magnetic field increases, more vortices are formed and the distance between vortices reduces. To pin more vortices, a higher density of nanocolumnar defects is required. As seen in Figure 3-10, a cross over happens at 5 T between 5 mol% Zr-doped (Gd, Y)BCO and 15 mol% Zr-doped (Gd, Y)BCO film, indicating that 15 mol% Zr-doped (Gd, Y)BCO starts dominating in fields higher than 5 T. At 65 K, 9 T ($B \parallel c$ -axis), 15 mol% Zr-doped (Gd, Y)BCO shows the highest J_c of 0.92 MA/cm^2 , which is $\sim$ two-fold higher than the J_c ($\sim 0.5 \text{ MA/cm}^2$) of the 5 mol% Zr-doped (Gd, Y)BCO film and $\sim$ five-

fold higher than the J_c ($\sim 0.19 \text{ MA/cm}^2$) of the undoped (Gd, Y)BCO film. The retention factor at 65 K, 9 T ($B \parallel c\text{-axis}$) [defined as the ratio of I_c at 65 K, 9 T ($B \parallel c\text{-axis}$) to I_c at 65 K, 0 T) for 15 mol% (Gd, Y)BCO is 0.62, which is much higher than the 0.17 and 0.05 retention factors of 5 mol% Zr-doped (Gd, Y)BCO and undoped (Gd, Y)BCO respectively.

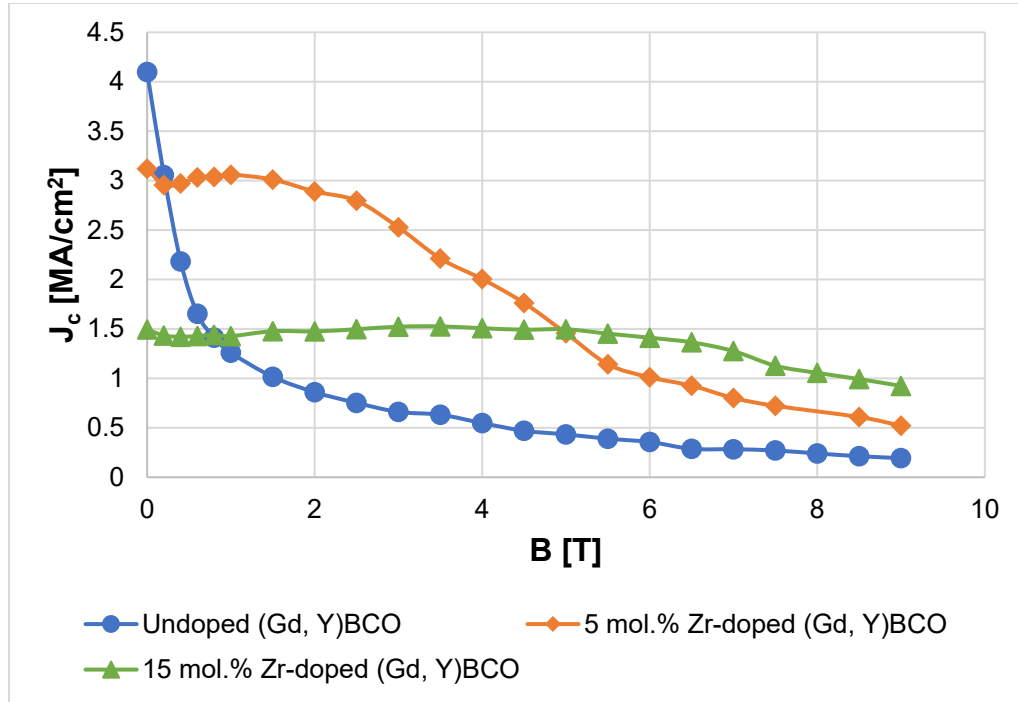


Figure 3-10. J_c of an undoped (Gd, Y)BCO film, and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO films at 65 K in magnetic fields up to 9 T applied along the c -axis.

Figure 3-11 shows TEM plan and cross-sectional views of 5 mol% Zr-doped (Gd, Y)BCO and 15 mol% Zr-doped (Gd, Y)BCO films. Figures 3-11 (a) and (b) show cross-sectional views of a 5 mol% Zr-doped (Gd, Y)BCO film with a thickness of $4.8 \mu\text{m}$, indicating long and continuous BaZrO_3 nanocolumns with BZO diameter varying with thickness. Horizontal thin arrows indicate BZO with smaller diameter ($\sim 3\text{-}5 \text{ nm}$) and thicker horizontal arrows points to bottle-shaped BZO ($\sim 8\text{-}16 \text{ nm}$). The reasons for this occurrence and the full effect of bottle-shaped BZO are still under study. Preliminary

studies revealed traces of rare-earth element in the bottle-shaped section, as described in a recent publication [111]. Some RE_2O_3 particles can be seen growing in the *ab* plane direction, indicated by vertical arrows in figure 3-11 (b). RE_2O_3 precipitates have smaller lattice mismatches with (Gd, Y)BCO and can readily nucleate at the surface of the growing REBCO film. These precipitates increase the self-field J_c and pinning near the *a-b* plane and in random orientations of applied magnetic field [86,87,92,113,114]. Figure 3-11 (c) shows a plan-view of a 5 mol% Zr-doped film indicating a random distribution of the smaller and larger diameter nanocolumns (bottle-shaped), mostly dominated by latter (as also seen in cross-section), with an average diameter and spacing of 9 nm and 22 nm respectively.

Figures 3-11 (d) and (e) show cross-sectional views of a 15 mol% Zr-doped (Gd, Y)BCO film with a thickness of 3.8 μm , indicating long, continuous, and more uniform nanocolumns along the cross-section. Some bottle-shaped BZO can still be seen but their periodicity is much less than the 5 mol% Zr-doped (Gd, Y)BCO. Also, there are no traces of RE_2O_3 precipitates. Figure 3-11 (f) shows a plan-view of 15 mol% Zr-doped (Gd, Y)BCO indicating a random distribution of the small- and large-diameter nanocolumns (bottle-shaped) with an average BZO diameter and spacing of 7 nm and 17 nm respectively. As the dopant concentration increases and Ba in the composition is compensated, BaZrO_3 self-assembles as vertically aligned and continuous nanocolumns parallel to the (Gd, Y)BCO *c*-axis and the density of nanocolumnar defects increases. The matching field, $B_\Phi = \Phi_0/a_0^2$ (where $\Phi_0 = 2.07 \times 10^{-15}$ Wb is the magnetic flux quantum and a_0 is the nanorod spacing) is the field at which the density of vortices matches that of the BZO nanocolumns [45,81,111] and is calculated to be ~ 4.2 T and ~ 7.2 T for the 5 mol% Zr-doped and 15

mol% Zr-doped (Gd, Y)BCO films respectively. The higher matching field of 15 mol% Zr-doped (Gd, Y)BCO indicates very strong pinning of the vortices.

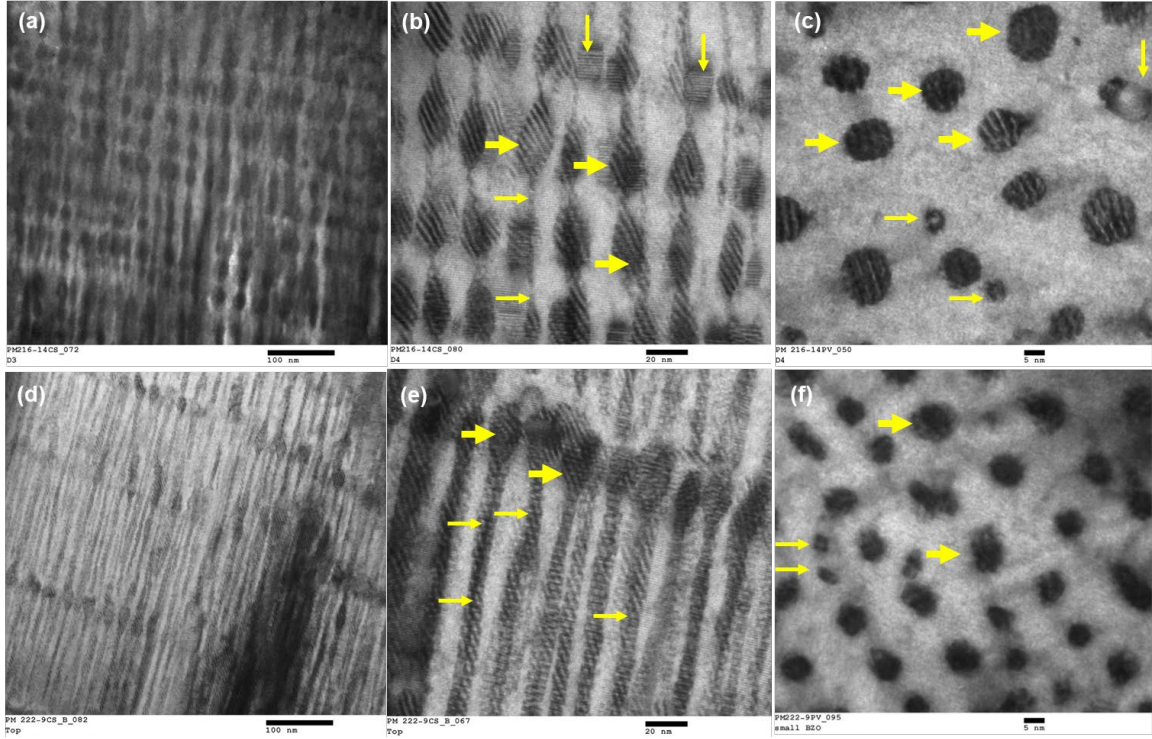


Figure 3-11. (a), (b) and (c) shows TEM cross-section, magnified cross-section and plan view of 5 mol% Zr-doped (Gd, Y)BCO respectively. (d), (e) and (f) shows the same for 15 mol% Zr-doped (Gd, Y)BCO.

To establish reproducibility and confirm the trend described above, more films of undoped (Gd, Y)BCO, 5 mol% Zr-doped (Gd, Y)BCO, and 15 mol% Zr-doped (Gd, Y)BCO were investigated using PPMS. Figure 3-12 shows the magnetic and transport J_c at 65 K, 1.5 T for different undoped, 5 mol% Zr-doped and 15 mol% Zr-doped (Gd, Y)BCO films. PPMS was used to obtain the magnetic J_c values, which show the same trend as transport J_c , although with different absolute values. PPMS uses a stricter criterion than the usual transport criterion of $1 \mu\text{V cm}^{-1}$, which explains the difference in their absolute values [117]. Also, in-field transport J_c is measured at $B \parallel c$ -axis while, in magnetic J_c

measurement, the magnetic field is perpendicular to the tape, not parallel to the c -axis of (Gd, Y)BCO. The transport J_c of a undoped (Gd, Y)BCO is $\sim 1 \text{ MA/cm}^2$ at 65 K, 1.5 T ($B \parallel c$ -axis) while the magnetic J_c is 0.46 MA/cm^2 ($B \perp$ tape). For 5 mol% Zr-doped (Gd, Y)BCO, five different films exhibited consistent magnetic J_c values at 65 K, 1.5 T ($B \perp$ tape) in the range of 1.72 to 1.76 MA/cm^2 while the transport J_c for three different 5 mol% Zr-doped (Gd, Y)BCO films lies between 2.9 and 3.3 MA/cm^2 . This follows the same trend as shown in Figure 3-10. By increasing nanocolumnar defects in 5 mol% Zr, a greater than 0.90 retention factor is obtained, thus maintaining a much higher J_c value compared with undoped (Gd, Y)BCO. Also, for 15 mol% Zr-doped (Gd, Y)BCO, four different films show consistent magnetic J_c s at 65 K, 1.5 T ($B \perp$ tape) in the range of 0.92 to 0.98 MA/cm^2 while the transport J_c for a 15 mol% Zr-doped (Gd, Y)BCO films is 1.5 MA/cm^2 , which is higher than undoped (Gd, Y)BCO but lower than 5 mol% Zr-doped (Gd, Y)BCO films. This confirms the trend shown in transport J_c and indicates that, at lower fields, such as 1.5 T ($B \parallel c$ -axis), 5 mol% Zr-doped (Gd, Y)BCO is best suited to achieve higher critical current capability.

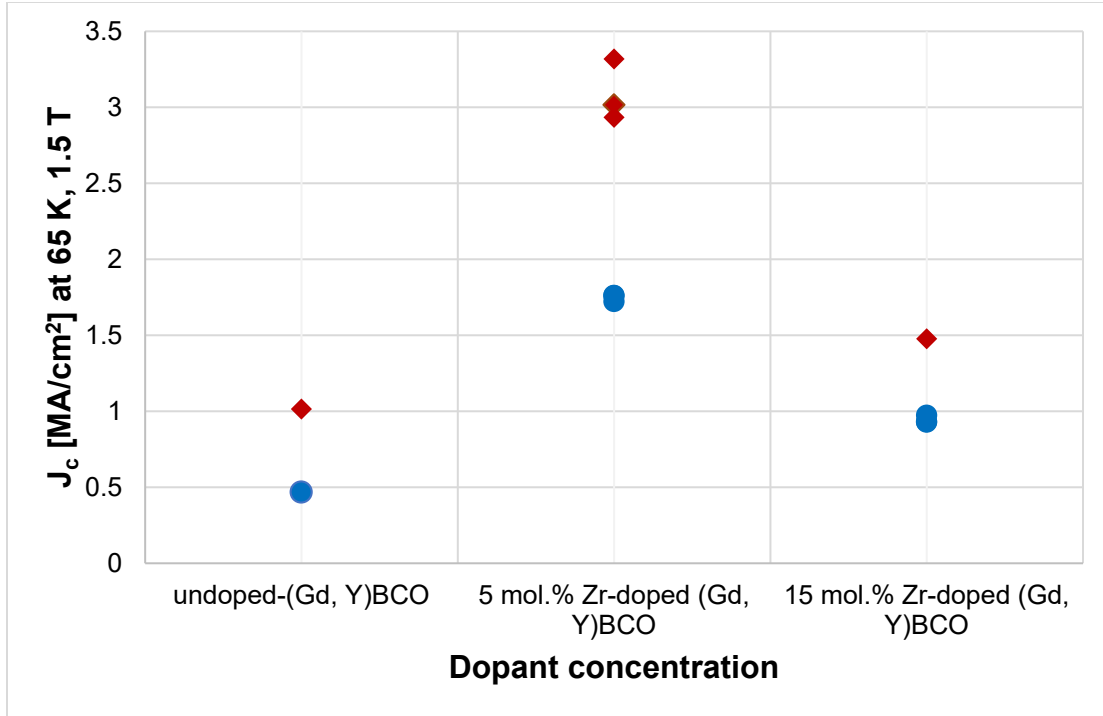


Figure 3-12. Transport (dark red-colored diamonds) and magnetic (blue-colored circles) J_c at 65 K, 1.5 T of thick undoped (Gd, Y)BCO films and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO films.

Figure 3-13 shows the magnetic and transport J_c at 65 K, 9 T for all the samples shown in Figure 3-12 for 65 K, 1.5 T. The transport J_c for a undoped (Gd, Y)BCO is ~ 0.2 MA/cm² at 65 K, 1.5 T ($B \parallel c$ -axis) while the magnetic J_c is 0.05 MA/cm² ($B \perp$ tape). Five different 5 mol% Zr-doped (Gd, Y)BCO films show magnetic J_c values at 65 K, 9 T ($B \perp$ tape) in the range of 0.28 to 0.32 MA/cm² while the transport J_c values for three of these films lie between 0.52 and 0.61 MA/cm². Also, for 15 mol% Zr-doped (Gd, Y)BCO, four different films show magnetic J_c values at 65 K, 1.5 T ($B \perp$ tape) in the range of 0.37 to 0.54 MA/cm² while the transport J_c for one of these film is 0.9 MA/cm².

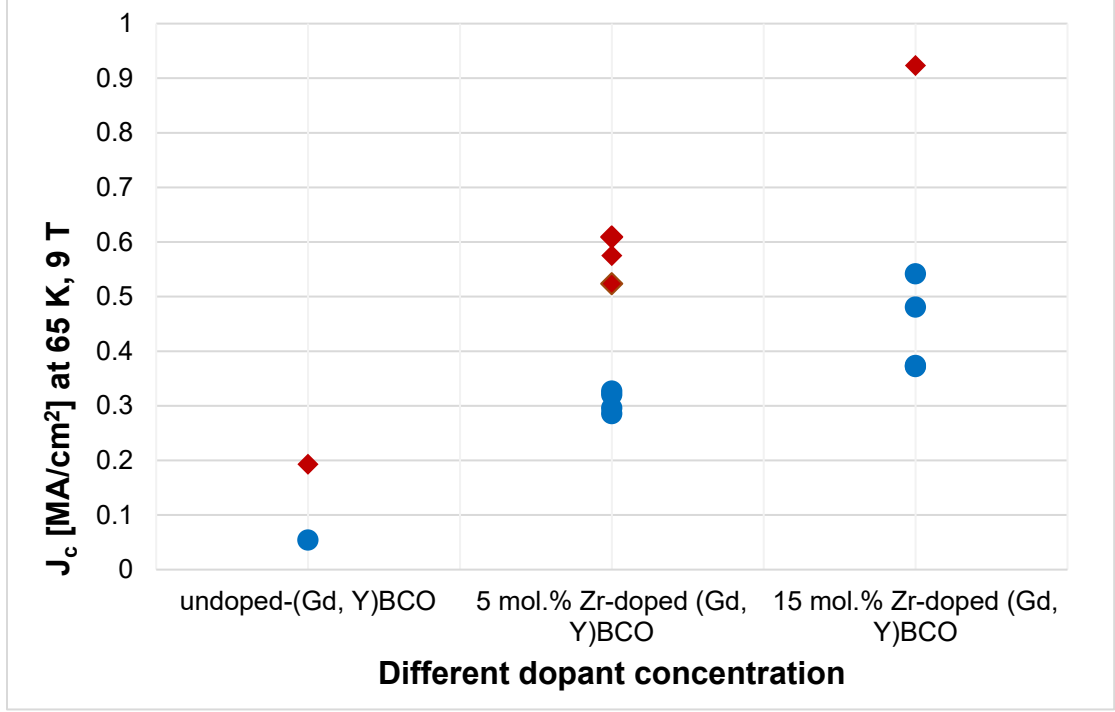


Figure 3-13. Transport (dark red-colored diamonds) and magnetic (blue-colored circles) J_c at 65 K, 9 T of thick undoped (Gd, Y)BCO films and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO films.

From these results, it is evident that obtaining high J_c in different fields ($B \parallel c$ -axis) at 65 K requires different pinning landscapes. For example, as shown in Figure 3-10, below 5 T, 5 mol% Zr-doped films demonstrates highest J_c while, above 5 T, 15 mol% Zr-doped films dominates. At self-field and the very low field of 0.2 T, undoped (Gd, Y)BCO shows higher J_c . This behavior can be simplified using two important metrics: (1) J_c at 77 K, 0 T and (2) lift factor (defined as the ratio of J_c at the desired temperature and field to J_c at 77 K, 0 T). $[J_c \text{ at } 65 \text{ K}, 1.5 \text{ T} (B \parallel c - \text{axis}) = J_c \text{ at } 77 \text{ K}, 0 \text{ T} \times [\frac{J_c \text{ at } 65 \text{ K}, 1.5 \text{ T}}{J_c \text{ at } 77 \text{ K}, 0 \text{ T}}]]$.

Lift factor indicates the pinning characteristics of the films. As seen in Table 3-3, lift factor at 65 K, 1.5 T ($B \parallel c$ -axis) increases with increasing density of nanocolumns, for example, its values are 0.46 for an undoped film, 2.17 for 5 mol% Zr-doped film and 2.31 for 15 mol% Zr-doped film. It is essential to consider that, at lower fields such as 1.5 T, 77

K, self-field dominates. Therefore, to reach a higher J_c at 65 K, 1.5 T ($B \parallel c$ -axis), a lower density of nanocolumns is preferable, which doesn't degrade self-field J_c by much when compared with high nanocolumn density. However, at higher fields, such as 9 T ($B \parallel c$ -axis), pinning dominates and, hence, high lift factor is more important and 15 mol% Zr-doped films have higher J_c values than 5 mol% Zr-doped films.

Table 3-3. Comparison of transport J_c at 77 K, 0 T; 65 K, 1.5 T ($B \parallel c$ -axis); 65 K, 9T ($B \parallel c$ -axis), and lift factor at 65 K, 1.5 and 9 T ($B \parallel c$ -axis) for undoped (Gd, Y)BCO and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO films.

	Transport J_c (MA/cm ²)	Transport J_c (MA/cm ²)	Transport J_c (MA/cm ²)	Transport Lift Factor	Transport Lift Factor
	77 K, 0 T	65 K, 1.5 T ($B \parallel c$ -axis)	65 K, 9 T ($B \parallel c$ -axis)	65 K, 1.5 T ($B \parallel c$ -axis)	65 K, 9 T ($B \parallel c$ -axis)
Undoped-(Gd, Y)BCO	2.23	1.02	0.19	0.46	0.09
5 mol% Zr-doped (Gd, Y)BCO	1.39	3.02	0.52	2.17	0.38
15 mol% Zr-doped (Gd, Y)BCO	0.64	1.48	0.92	2.31	1.45

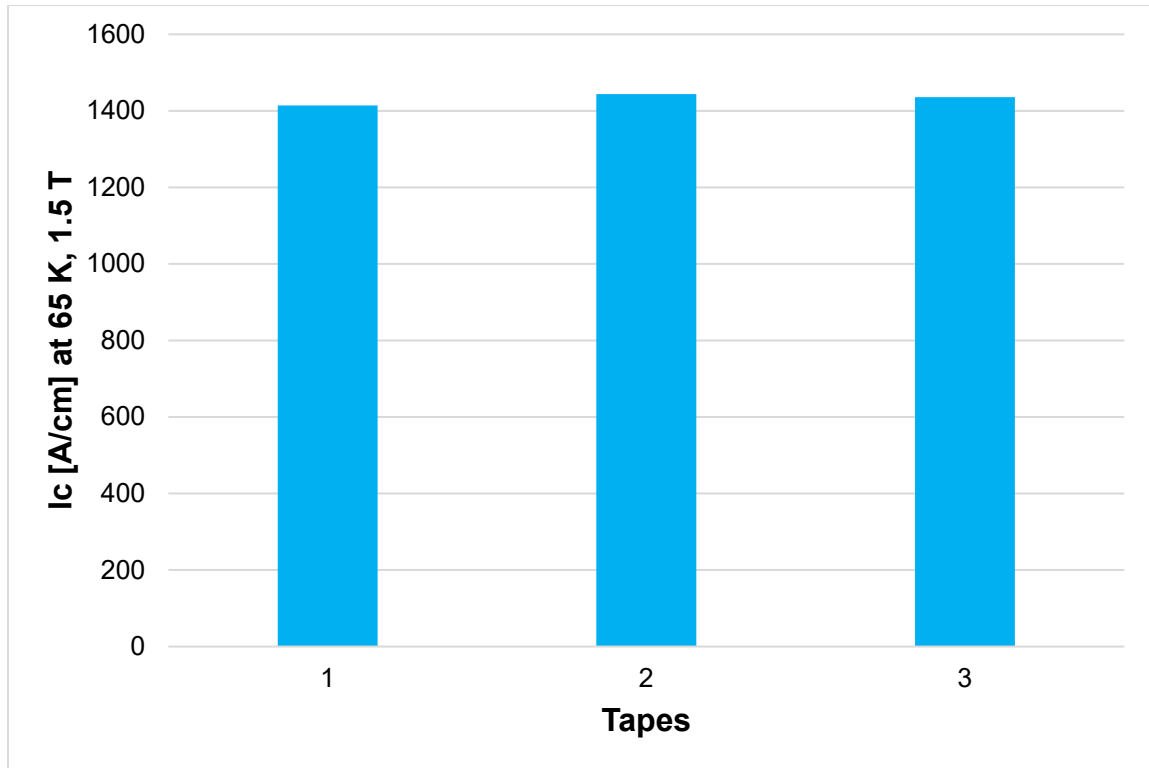


Figure 3-14. Critical current (A/cm) of three different 5 mol% Zr-doped (Gd, Y)BCO film thicknesses (5.1, 4.35, and 4.8 μm) at 65 K in magnetic fields of 1.5 T applied along the c -axis. All films used 0.025 M precursors for their deposition.

Minimum J_c is an important performance parameter for wound wire architecture devices such as high field magnets, motors, and generators [115]. Figure 3-15 shows the angular dependence of critical current over a magnetic field orientation of -100° to 30° to the tape normal at 65 K, 1.5 T for the same samples as shown in Figure 3-10. The undoped (Gd, Y)BCO film appears more isotropic with a $B \parallel ab$ peak at 0.88 MA/cm^2 and min. J_c at 0.53 MA/cm^2 . The $B \parallel a-b$ peak indicates the presence of $a-b$ plane in-plane precipitates, such as RE_2O_3 particles, which enhances pinning. While there is no abrupt occurrence of any peak near the $B \parallel c$ -axis, the overall J_c near 10° shows a max. J_c of 1.1 MA/cm^2 . This undoped film was checked by ICP-MS to confirm that there were no traces of dopants in the film. Initial results have hinted that occurrence of max. J_c near 10° can be attributed to

thickness but these studies are still underway. 5 mol% Zr-doped film shows a very sharp and high peak of $\sim 3 \text{ MA/cm}^2$ at the $B \parallel c$ -axis, with a min. J_c of 0.38 MA/cm^2 and a small a-b plane peak at 0.56 MA/cm^2 . The maximum J_c of 15 mol% Zr-doped film shows a sharp peak of 1.48 MA/cm^2 at $B \parallel c$ -axis with a min. J_c of 0.16 MA/cm^2 and almost no a-b plane peak. The occurrence of an a-b plane peak in 5 mol% Zr-doped film can be attributed to RE_2O_3 precipitates, as seen in Figure 3-11(b).

Anisotropy increases with increasing dopant concentration as seen from tabulated values in Table 3-4, anisotropy ratio (= maximum J_c /minimum J_c) is 2.1 in an undoped film and increases to a very high ratio of 7.9 for the 5 mol% Zr-doped film. The reason behind this is the formation of nanocolumnar defects, which did improve pinning at the $B \parallel c$ -axis to a record high value of over 1440 A/cm at 65 K, 1.5 T but decreased the overall self-field J_c , due to the increased c -lattice constant and texture degradation, which likely led to a reduction in the min. J_c at 65 K, 1.5 T. The anisotropy ratio further increased to 9.1 with increasing dopant concentration up to 15 mol%, which is due to further increases in the density of nanocolumnar defects while degrading the self-field J_c by a large margin.

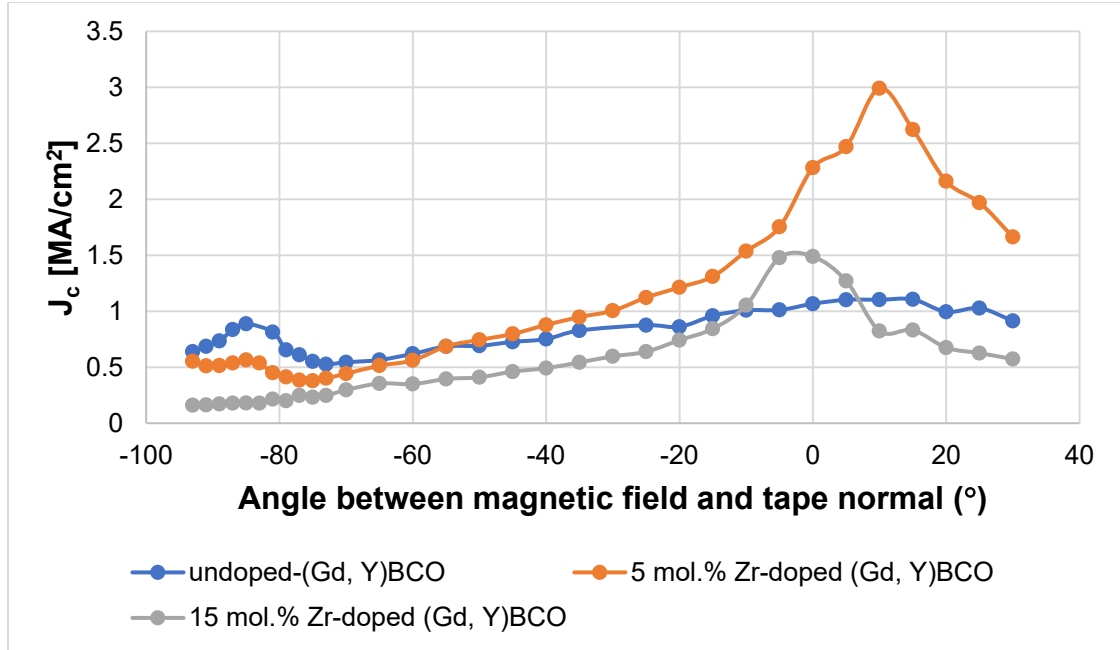


Figure 3-15. Angular dependence of J_c for an undoped thick (Gd, Y)BCO film and Zr-doped (5 mol% and 15 mol%) thick (Gd, Y)BCO film at 65 K in 1.5 T magnetic field.

Table 3-4. Comparison of minimum J_c , maximum J_c and anisotropy at 65 K, 1.5 T for an undoped and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO films.

	Thickness (μm)	Min. J_c at 65 K, 1.5T (MA/cm ²)	Max. J_c (c-peak) at 65 K, 1.5T (MA/cm ²)	$B_{\parallel}$ ab peak at 65 K, 1.5 T (MA/cm ²)	Anisotropy (max./min.)
Undoped (Gd, Y)BCO	3.8	0.52	1.106	0.88	2.1
5 mol% Zr-doped (Gd, Y)BCO	4.8	0.38	2.99	0.56	7.9
15 mol% Zr-doped (Gd, Y)BCO	3.8	0.163	1.48	0.248	9.1

3.2.2. Improving isotropic pinning properties of 5 mol% doped (Gd, Y)BCO films at 65 K, in magnetic fields of 1.5 T and 0.25 T.

Section 3.2.1. clearly indicates that for applications at 65 K, lower fields and lower dopant concentrations (5 mol% Zr-doped (Gd, Y)BCO) are preferred over both undoped (Gd, Y)BCO and high dopant concentrations [15 mol% Zr-doped (Gd, Y)BCO]. However,

as shown in Table 3-4, the anisotropy ratio (max. J_c /min. J_c) for 5 mol% Zr-doped (Gd, Y)BCO is ~ 8 , which is a very high ratio for wound wire architecture applications. Therefore, it is essential to improve the min. J_c while not considerably degrading the J_c (B || c -axis).

Three different studies were done to address the high anisotropy of 5 mol% doped (Gd, Y)BCO films.

3.2.2.1. The effect of molarity on the microstructural and transport properties of 5 mol% zirconium (Zr)-doped (Gd, Y)BCO film

One of the ways to reduce anisotropy is to break the nanocolumnar defects into small pinning centers and make them grow in random directions to improve pinning at all angles except the B || c -axis. Although this will reduce the pinning properties in the c -axis direction, it should improve the minimum J_c . To do this, one factor to investigate is increasing the deposition rate. Some research groups have suggested that increasing deposition rate to a very high level increases surface roughness and decreases the crystallinity of the film accompanied by the formation of a -axis-oriented grains [118,119]. Increasing the surface roughness to a certain limit where it doesn't degrade the self-field J_c of (Gd, Y)BCO films too much while still disrupting some nanorods may work for our purpose. Therefore, it is important to confirm the effect of molarity, especially for thick films, to understand its effect on critical current and microstructural properties.

3.2.2.1.1. The effect of precursor molarity on microstructure and self-field transport critical current density at 77 K

Table 3-5 shows the precursor molarity, thickness, deposition rate, and transport self-field critical current density at 77 K. The deposition rate increases from 0.12 $\mu\text{m}/\text{min}$ for 0.025 M to 0.79 $\mu\text{m}/\text{min}$ for 0.15 M. This is expected: when the molarity of the precursor increases, the concentration of precursor elements in the solution increases, which enhances the deposition rate. This increase in deposition rate, after a certain level, adversely impacts the critical current properties, as seen by the drop in self-field critical current density. Critical current density at 77 K, 0 T stays almost constant with a value of 1.3-1.5 MA/cm^2 for 0.025 to 0.075 M but then decreases sharply to 0.8 MA/cm^2 for 0.1 M and then to 0.6 MA/cm^2 for 0.15 M. The main reason behind this decrease is the increased misoriented *a*-axis grains formed at a higher deposition rate. Increases in *a*-axis grains can lead to high-angle grain boundaries, which can degrade the current passing along the *a*-*b* plane.

Table 3-5. Comparison of deposition rate and transport self-field J_c at 77 K for 5 mol% Zr-doped (Gd, Y)BCO tapes made with different precursor molarities from 0.025 to 0.15 M.

Thickness [μm]	Precursor Molarity	Deposition rate [$\mu\text{m}/\text{min}$]	Transport J_c at 77 K, 0 T [MA/cm^2]
5.1	0.025 M	0.12	1.3
5.3	0.05 M	0.22	1.5
5.5	0.075 M	0.34	1.3
6.3	0.1 M	0.52	0.8
6.3	0.15 M	0.79	0.6

Figure 3-16(a) to (e) shows the plane and cross-sectional view of five different 5 mol% Zr-doped (Gd, Y)BCO films made using 0.025 M, 0.05 M, 0.075 M, 0.1 M, and 0.15 M respectively. The inset image of each figure shows a cross-sectional view of same film.

The surface morphology and cross-section of 0.025 M and 0.05 M shown in Figures 3-16(a) and (b) respectively indicates almost negligible occurrence of *a*-axis-oriented grains and also shows very uniform cross-section without any cracks, porosity, or secondary phases. This indicates good, uniform growth conditions across the whole thickness of the film. This relates well with the consistent and high transport self-field critical current density (J_c), as shown in Table 3-5. Figure 3-16(c) with 0.075 M shows relatively higher amounts of *a*-axis-oriented grains, reflecting the effect of a higher deposition rate. A cluster of *a*-axis-oriented grains is indicated by a horizontal arrow and some random, misoriented grains are shown by vertical arrows. The cross-section was taken at an *a*-grains-free location, hence the roots of the *a*-grains are not evident. The transport J_c is still in the acceptable range but these misoriented grains do affect the continuous growth of the nanorods, which will be reflected in the in-field properties. Figures 3-16(d) and (e) deposited using 0.1 M and 0.15 M precursors respectively, show the formation of large amounts of misoriented *a*-axis grains, which can be observed both on the surface as well as in the cross-section. The cross-sectional view of both films shows that *a*-axis grains have roots that reached the substrate, thus indicating the loss in crystallinity in the film from the nucleation itself. Secondary phases and *a*-axis-oriented grains can hinder the current transport properties of the film along the *a*-*b* plane and, hence, cause degradation in self-field J_c at 77 K, 0 T, as shown in Table 3-5. It is very difficult to understand the growth mechanism of (Gd, Y)BCO due to the presence of different elements with different diffusion coefficients, which affects the growth kinetics. However, according to the growth kinetic model proposed by Trofimov et al., for single element materials, the surface roughness is determined by a single dimensionless parameter, which is proportional to the

ratio of the surface diffusion coefficient and deposition flux [120]. With increasing deposition rate, the growth mechanism goes from smooth two-dimensional layer-by-layer growth to rough multilayer growth.

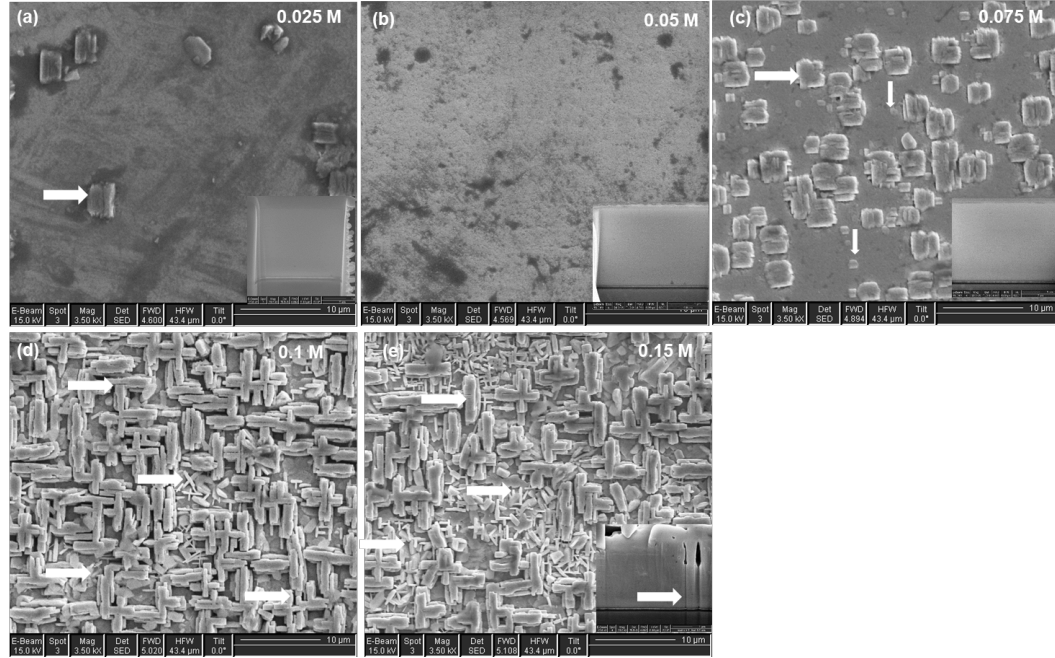


Figure 3-16. SEM plane view and FIB cross-section (inset) of 5 mol% Zr-doped (Gd, Y)BCO thick tapes made using different molarity of precursor: (a) 0.025 M, (b) 0.05 M, (c) 0.075 M, (d) 0.1 M, (e) 0.15 M.

Figures 3-17(a) to (e) show the pole figures of (Gd, Y)BCO (103) peak for 5 mol% Zr-doped films made using different precursor molarities (0.025 M, 0.05 M, 0.075 M, 0.1 M, and 0.15 M). All samples show (Gd, Y)BCO (103) peaks indicating the formation of a (Gd, Y)BCO phase at each molarities. Films deposited with 0.025 M and 0.05 M show very sharp (00l) peaks indicating a high degree of orientation in the a-b plane. However, as the molarity increases, the (Gd, Y)BCO (103) peak starts to streak in the phi direction, as shown by the arrows in Figures 3-17 (c) to (e) indicating the formation of misoriented grains. This streaking increases as the molarity is increased from 0.075 M to 0.1 M and becomes a visible ring in the phi direction. This streaking in the phi direction indicates

random misoriented grains. Also, the four-fold symmetry of the films seems to get worse. This is attributed to the deterioration of the films' crystallinity from the increase in surface roughness of the films with increasing deposition rates.

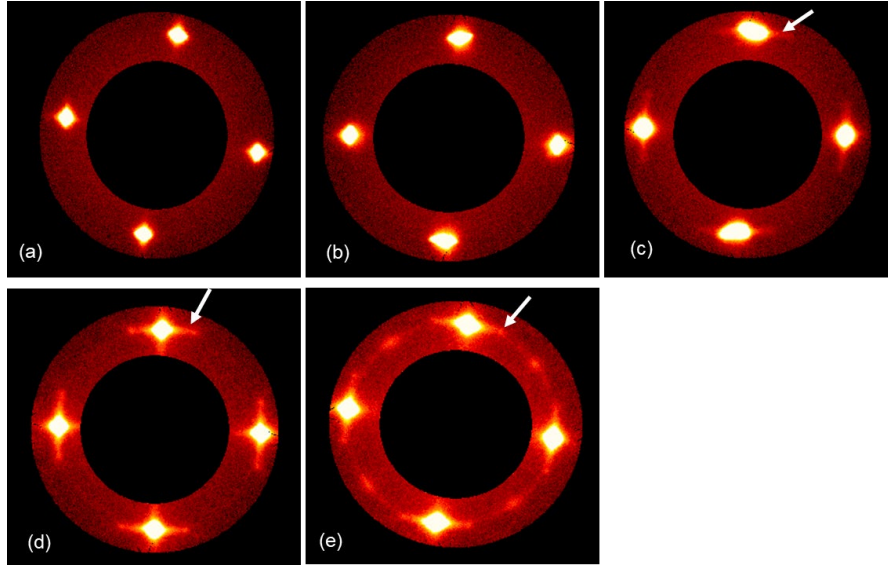


Figure 3-17. (Gd, Y)BCO (103) XRD pole figure of 5 mol% Zr-doped (Gd, Y)BCO films made using different molarity precursors: (a) 0.025 M, (b) 0.05 M, (c) 0.075 M, (d) 0.1 M, (e) 0.15 M. Streaking direction is indicated by arrows.

3.2.2.1.2. The effect of molarity on in-field critical current density

The critical current density (J_c) angular dependence at 65 K in 1.5 T magnetic field of five different 5 mol% Zr-doped (Gd, Y)BCO films with molarities of 0.025 M, 0.05 M, 0.075 M, 0.1 M, and 0.15 M is shown in Figure 3-18. (Gd, Y)BCO films with 0.025 M and 0.05 M have very similar J_c values of 2.7 and 2.8 MA/cm² respectively at an angle where the magnetic field is parallel to the c -axis ($B \parallel c$ -axis) of (Gd, Y)BCO indicating that, up to 0.05 M, a similar density of nanocolumns grows across the whole thickness of the films without being affected by approximately doubling the deposition rate. Also, a very similar minimum J_c between 0.5 – 0.6 MA/cm² was achieved, showing that in-plane precipitates, such as RE₂O₃ or other random defects, are similar in films deposited with 0.025 and 0.05

M. 0.075 M films show a slightly higher minimum J_c of 0.67 MA/cm² but a lower J_c of 2.4 MA/cm² at the $B \parallel c$ -axis of (Gd, Y)BCO. The increase in minimum J_c can be due to an increase in the density of in-planar defects. Also, these in-planar defects can break the continuously growing BaZrO₃ nanocolumns and, hence, decrease its J_c at $B \parallel c$ -axis. (Gd, Y)BCO films with 0.1 M and 0.15 M show an almost constant J_c at all angles except for small peaks with J_c of around ~ 0.5 MA/cm² near the $B \parallel ab$ plane. This peak indicates the presence of in-planar defects. No peak along the $B \parallel c$ -axis indicates the absence of nanocolumn formation, which relates well to the surface morphology shown in Figure 3-17 depicting a high density of a -axis-oriented grain formation and secondary phases. Also, the overall drop in J_c at 1.5 T for 0.1 M and 0.15 M is due to the drop in its self-field critical current density because of the high density of a -axis-oriented grains blocking the transport current flow.

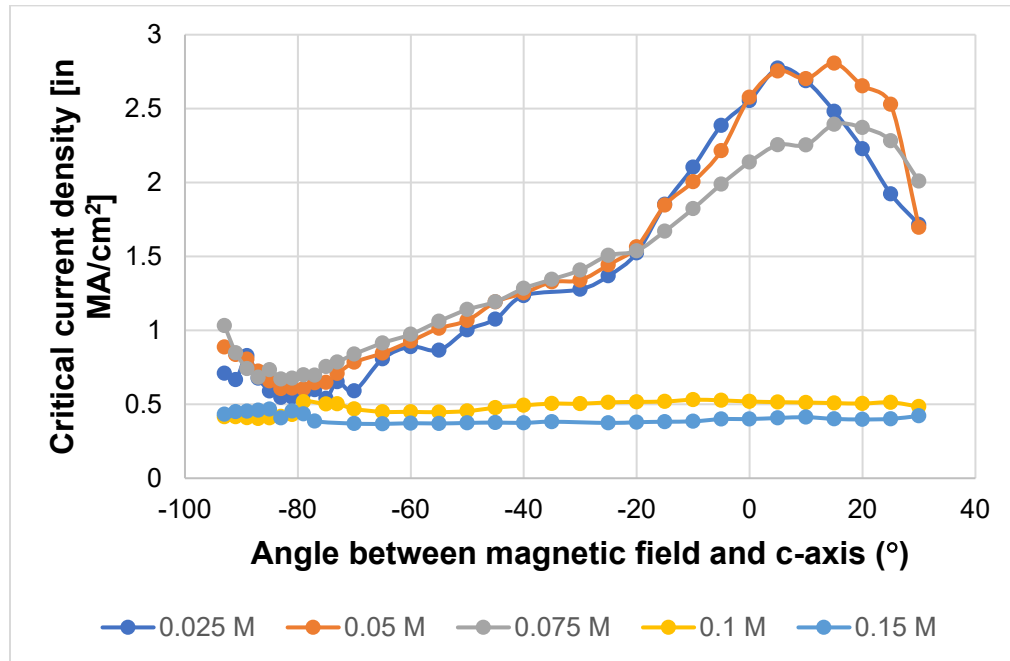


Figure 3-18. Angular dependence of critical current density (J_c) for 5 mol% Zr-doped (Gd, Y)BCO films with precursor molarities of 0.025 M, 0.05 M, 0.075 M, 0.1 M, and 0.15 M at 65 K in a 1.5 T magnetic field.

It is evident from the above results that increasing molarity is not beneficial to noticeably increase the min. J_c . Although 0.075-M films do show a slight improvement in isotropic behavior, this is still far from the desired outcome.

3.2.2.2. The effect of different dopant (Hf) at low concentration (5 mol%)

Several research groups have shown that (Gd, Y)BCO doped with low concentrations of Hf exhibits a better isotropic behavior at high temperatures and low fields [49,68,70,79,95,121]. At low concentrations, BHO seems to form discontinuous nanorods in a splayed orientation with a smaller diameter and less spacing (higher density), which seems to prevent the high degradation of self-field J_c of (Gd, Y)BCO, as was evident in the 5 mol% Zr-doped (Gd, Y)BCO sample, which allows for a higher minimum J_c with much lower anisotropy. Here, 5 mol% Hf-doped thick (Gd, Y)BCO films with two different Ba concentrations in their compositional ratios were studied. Two different 5 mol% Zr-doped (Gd, Y)BCO films, 4.35 μm and 4.8 μm thick, were grown in a single deposition using A-MOCVD with a precursor compositional ratio of $\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_2\text{Cu}_{2.60}\text{Zr}_{0.05}$. Two different 5 mol% Hf-doped (Gd, Y)BCO films with thicknesses $\sim 4.8 \mu\text{m}$ were grown in a single deposition with a precursor compositional ratio of $\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{1.87}\text{Cu}_{2.60}\text{Hf}_{0.05}$. Another two 5 mol% Hf-doped (Gd, Y)BCO films with thicknesses $\sim 4.3 \mu\text{m}$ were grown in a single deposition with a precursor compositional ratio of $\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{1.92}\text{Cu}_{2.60}\text{Hf}_{0.05}$. All films were grown with 0.025 M precursors. For ease of readability, the following short forms for the given composition type is used in this section:

5% Zr-A – 5 mol% Zr-doped (Gd, Y)BCO films with precursor compositional ratio of $\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_2\text{Cu}_{2.60}\text{Zr}_{0.05}$

5% Hf-A - 5 mol% Hf-doped (Gd, Y)BCO films with precursor compositional ratio of $Y_{0.65}Gd_{0.65}Ba_{1.87}Cu_{2.60}Hf_{0.05}$

5% Hf-B - 5 mol% Hf-doped (Gd, Y)BCO films with precursor compositional ratio of $Y_{0.65}Gd_{0.65}Ba_{1.92}Cu_{2.60}Hf_{0.05}$

3.2.2.2.1. Transport self-field (0 T) J_c at 77 K of 5 mol% Hf-doped (Gd, Y)BCO

Shown in Figure 3-19 is the transport self-field J_c at 77 K of two 4- μ m films each of 5% Zr-A films with [(Ba-Zr)/Cu $\sim$ 0.66], 5% Hf-A films with [(Ba-Hf)/Cu $\sim$ 0.67] and 5% Hf-B films with [(Ba-Hf)/Cu $\sim$ 0.69]. The interpretation of the ratio is given below:

$$\frac{BaR}{Cu} = \frac{Ba - M}{Cu}$$

where, BaR – residual Ba in the (Gd, Y)BCO matrix (atomic percentage), Cu – copper-normalized concentration obtained from ICP-MS (at%), Ba – total Ba-normalized concentration obtained from ICP-MS (at%), M – normalized dopant (Hf or Zr) concentration obtained from ICP (at%).

Generally, dopants including Zr and Hf form only one phase, for example, BaZrO₃ and BaHfO₃ respectively, when used with (Gd, Y)BCO precursors for depositing thin high-temperature superconductor films. It is assumed that the amount of these dopants detected by ICP-MS will consume the same amount of Ba (at a ratio of 1:1) from the total Ba detected in the ICP-MS to form BZO or BHO nano defects (nanocolumns or nanodots) and that the rest of the Ba will be used to form the (Gd, Y)BCO matrix. 5% Hf-A with (Ba-Hf)/Cu $\sim$ 0.67, which is slightly copper deficient (or Ba excessive) in the (Gd, Y)BCO matrix, consistently shows more than 60% higher self-field J_c with absolute values of 1.93 - 2 MA/cm² when compared with self-field J_c of $\sim$ 1.2 MA/cm² for 5% Zr-A. Also, (Ba-

Zr)/Cu ~ 0.66 has the perfect stoichiometry of Ba:Cu being 2:3 compared with (Ba-Hf)/Cu ~ 0.67 where copper is deficient (or Ba is in excess). When increasing Ba in the Hf-doped (Gd, Y)BCO films such as in case of 5% Hf-B films with (Ba-Hf)/Cu ~ 0.69 , there is a decrease of 77 K, self-field J_c to ~ 1.80 MA/cm², which is still over 45% higher than that of 5% Zr-A films.

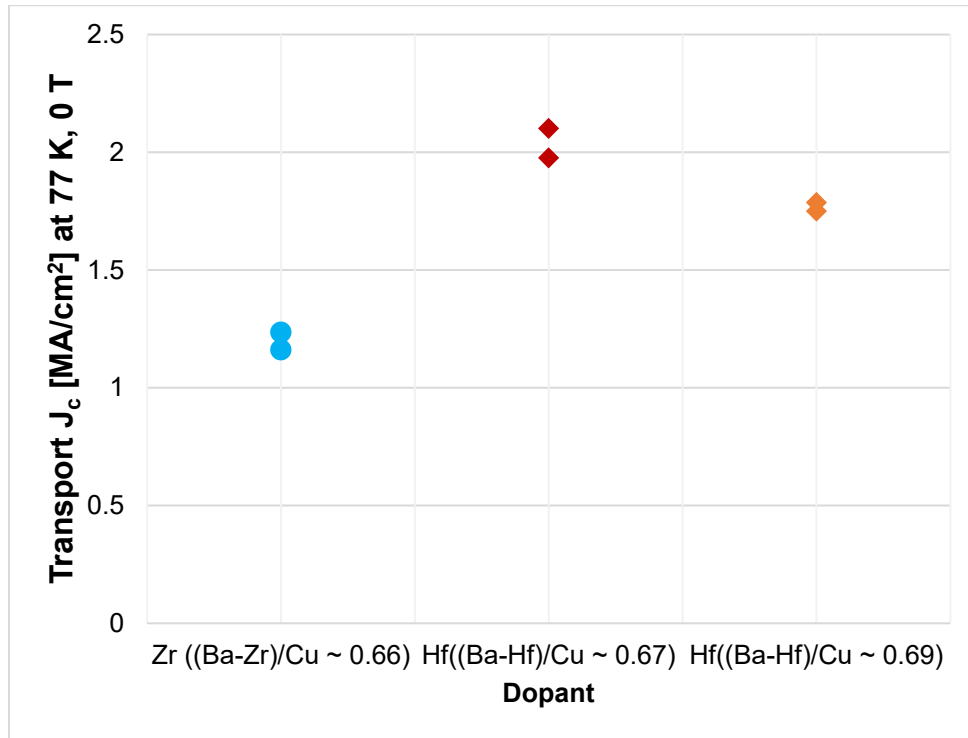


Figure 3-19. Transport J_c at 77 K, 0 T for 5 % Zr-A films with (Ba-Zr)/Cu ~ 0.66 , 5 % Hf-A films with (Ba-Hf)/Cu ~ 0.67 and 5 % Hf-B films with (Ba-Hf)/Cu ~ 0.69 .

It is important to try to understand the reason behind this higher self-field J_c with Hf doping. Therefore, the c -lattice parameters of all samples mentioned in Figure 3-19 were determined from the (00 l) peaks using a least-squares fit to the Nelson-Riley function, as shown in Figure 3-20 [105]. The c -axis lattice parameter of (Gd, Y)BCO for 5% Hf-A and 5% Hf-B films is consistently ~ 11.72 Å independent of the (Ba-Hf)/Cu ratio, which is lower than the c -axis lattice parameter (11.737 Å) of 5 % Zr-A films. Reductions in the

c-lattice parameter of (Gd, Y)BCO validate the increase in self-field J_c from 5 mol% Zr-doped films to 5 mol% Hf-doped films, as reductions in the *c*-lattice parameter reduce the distance between the strongly conducting CuO planes in (Gd, Y)BCO, hence increasing the charge concentrations and increasing the J_c . It is important to note that, although the *c*-lattice constant of 5% Hf-A and 5% Hf-B films is lower than the *c*-lattice constant of 5% Zr-A films, their BaR/Cu ratio does not decrease with a smaller *c*-lattice constant, as seen in Zr-doped films, in which lattice constant decreases with decreasing a similar ratio of (Ba+Zr)/Cu [122]. Also, when increasing the BaR/Cu ratio in Hf-doped films, there is no change observed in the *c*-axis constant; however, there is a slight decrease in the self-field J_c . To understand this phenomenon, it is important to examine the entire film composition. Table 3-6 shows the ICP-MS results of the samples illustrated in Figure 3-20. Two samples each of 5% Zr-A, 5% Hf-A and 5% Hf-B films were evaluated. 5 % Zr-A films with a precursor compositional ratio of $Y_{0.65}Gd_{0.65}Ba_2Cu_{2.60}Zr_{0.05}$ shows (Ba-Zr)/Cu $\sim$ 0.65-0.66 while 5% Hf-A with a precursor compositional ratio of $Y_{0.65}Gd_{0.65}Ba_{1.87}Cu_{2.60}Hf_{0.05}$ shows (Ba-Hf)/Cu $\sim$ 0.67 and 5% Hf-B films with a precursor compositional ratio $Y_{0.65}Gd_{0.65}Ba_{1.92}Cu_{2.60}Hf_{0.05}$ shows (Ba-Hf)/Cu $\sim$ 0.68 – 0.70. Ba in the precursor compositional ratio for 5 % Hf-A and 5% Hf-B are lower, 1.87 and 1.92 compared with a Ba of 2.00 in the precursor compositional ratio for 5% Zr-A films. With decreased Ba in the precursor compositional ratio from 2.00 in 5% Zr-A to 1.87 in 5% Hf-A, the Ba decreases in the film from 31.68 - 31.82 (at%) to 31.12 - 31.16 (at%). This decrease in Ba is expected, but surprisingly a large decrease in copper (at%) is seen and a surge in at% of rare-earth (Y+Gd) has been observed. Increase in rare-earth and decrease in Ba(at%) and copper (at%) in Hf-doped (Gd, Y)BCO indicates that the amount of RE₂O₃ precipitates

will be enhanced as the rare-earth required to form the Y123 phase will be less. Re_2O_3 has a good in-plane lattice match to the (Gd, Y)BCO phase and can readily nucleate at the surface of the growing REBCO film [87,112]. Due to fewer lattice mismatches, the heteroepitaxial growth of RE_2O_3 generates small misfit dislocations and can cause local lattice distortions in the (Gd, Y)BCO matrix, which can improve the pinning in random orientations and the ab plane [87]. The main advantage of RE_2O_3 precipitates is to improve the self-field J_c and in-field performance at lower fields, as shown in the literature [87,112–114,123]. This increase in RE_2O_3 precipitates in Hf-doped (Gd, Y)BCO films affirms the increase in self-field J_c at 77 K. The reason for the decrease in copper (at%) is still unclear but it seems that, with Hf doping, the incorporation of copper in the film is reduced. Also, the conversion of Zr beta diketonate from precursor to film (at%) seems to be distinctively higher than the conversion of Hf beta diketonate from precursor to film. In Figure 3-21, it is seen that the rare-earth (at%) to Ba (at%) ratio increases for Hf-doped films compared with Zr-doped films, in the same manner as the transport self-field J_c shown in Figure 3-19. Furthermore, between Hf-doped films, with increasing Ba, the rare-earth to Ba ratio decreases from 0.72 to 0.71, which is a similar trend to that observed in Figure 3-19 for the transport 77 K self-field J_c .

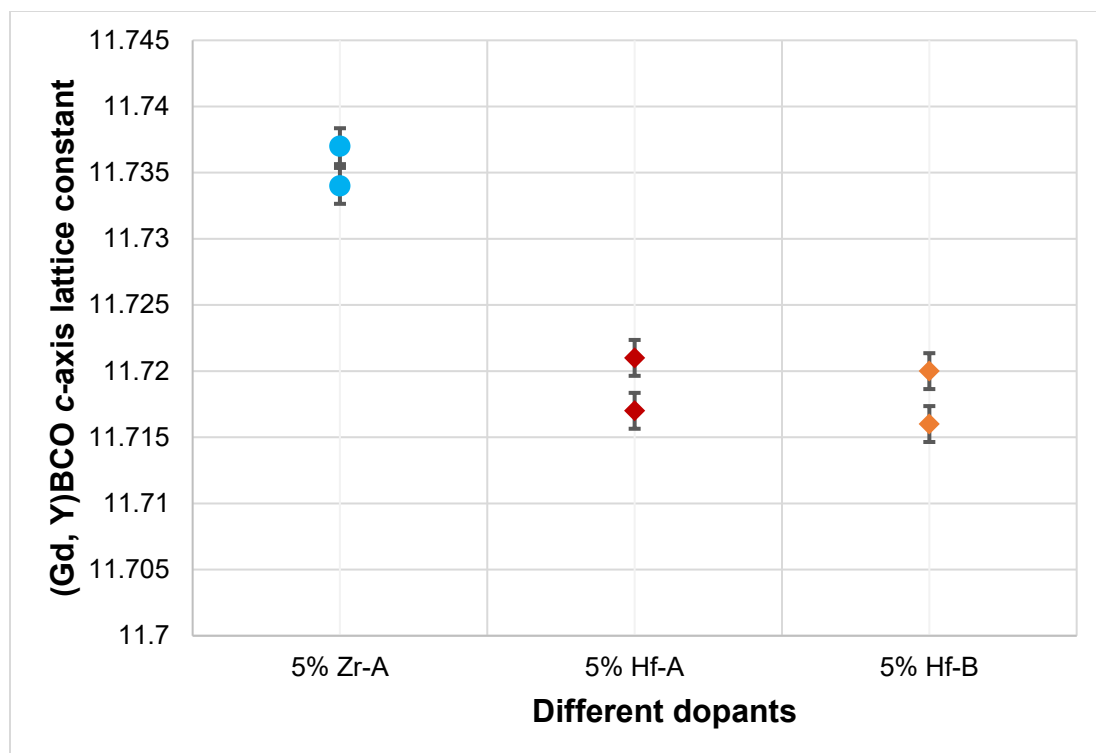


Figure 3-20. (Gd, Y) BCO *c*-lattice parameter of two samples each for 5 % Zr-A, 5 % Hf-A and 5 % Hf-B films.

Table 3-6. Comparison of composition obtained using ICP-MS (at%) for 5 % Zr-A, 5 % Hf-A and 5 % Hf-B films.

		Cu (at%)	Y (at%)	Zr or Hf (at%)	Ba (at%)	Gd (at%)	RE(Y+Gd) (at%)	(Ba- M)/Cu
5% Zr-A	$Y_{0.65}Gd_{0.65}Ba_2Cu_{2.60}Zr_{0.05}$	47.86	9.71	0.45	31.82	10.16	19.87	0.66
5% Zr-A	$Y_{0.65}Gd_{0.65}Ba_2Cu_{2.60}Zr_{0.05}$	48.09	9.64	0.46	31.68	10.13	19.77	0.65
5% Hf-A	$Y_{0.65}Gd_{0.65}Ba_{1.87}Cu_{2.60}Hf_{0.05}$	45.82	11.41	0.42	31.12	11.21	22.62	0.67
5% Hf-A	$Y_{0.65}Gd_{0.65}Ba_{1.87}Cu_{2.60}Hf_{0.05}$	45.90	11.32	0.41	31.16	11.19	22.51	0.67
5% Hf-B	$Y_{0.65}Gd_{0.65}Ba_{1.92}Cu_{2.60}Hf_{0.05}$	45.59	11.28	0.39	31.58	11.14	22.42	0.68
5% Hf-B	$Y_{0.65}Gd_{0.65}Ba_{1.92}Cu_{2.60}Hf_{0.05}$	45.19	11.23	0.38	31.91	11.28	22.51	0.70

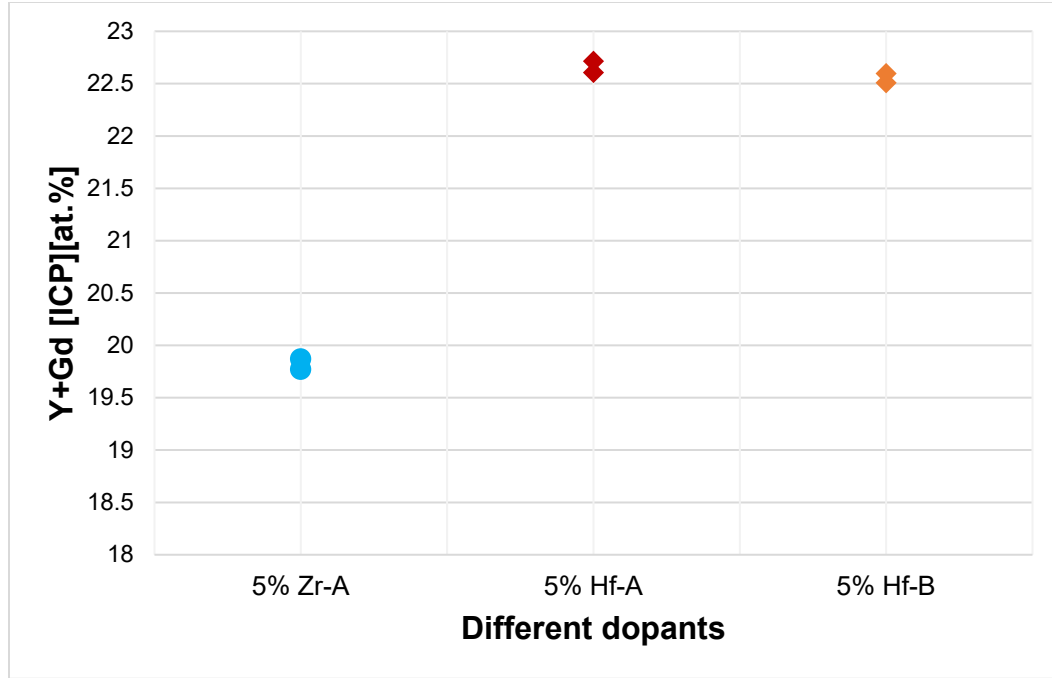


Figure 3-21. Ratio of rare-earth (Y+Gd) (at%) to Ba (at%) obtained using ICP-MS of two samples each for 5 % Zr-A, 5 % Hf-A and 5 % Hf-B films.

To further investigate RE_2O_3 precipitate formation and its effect on nanorod growth in 5% Hf-A films with $(\text{Ba-Hf})/\text{Cu} \sim 0.67$, TEM analysis was performed on cross-sections, as shown in Figure 3-22. Figure 3-22(a) shows the whole cross-sectional microstructure of the film, revealing a high density of RE_2O_3 precipitates forming along the a-b plane or at some small angle to the a-b plane, in plate as well as particle form. Some voids and secondary phases are also visible. Figure 3-22(b) clearly shows discontinuous BaHfO_3 with very small diameter (2.5-4 nm) growing along the *c*-axis (Gd, Y)BCO. BHO nanorods are breaking due to the large amount of RE_2O_3 precipitates. It seems that using Hf as the dopant (at a lower concentration), reduces the copper conversion from precursor to film, increasing the rare-earth relative content. This increase in rare-earth gives rise to more RE_2O_3 precipitates that break the nanorods leading to a moderate decrease in the *c*-lattice constant (compared with Zr-doped (Gd, Y)BCO film with continuous nanorods shown in Figure 3-

11(a) and (b), since continuous nanorods induces more positive strain in the REBCO matrix and increases the c -lattice constant. Decreased c -lattice constants and increased RE_2O_3 precipitates are favorable toward increasing self-field J_c at 77 K.

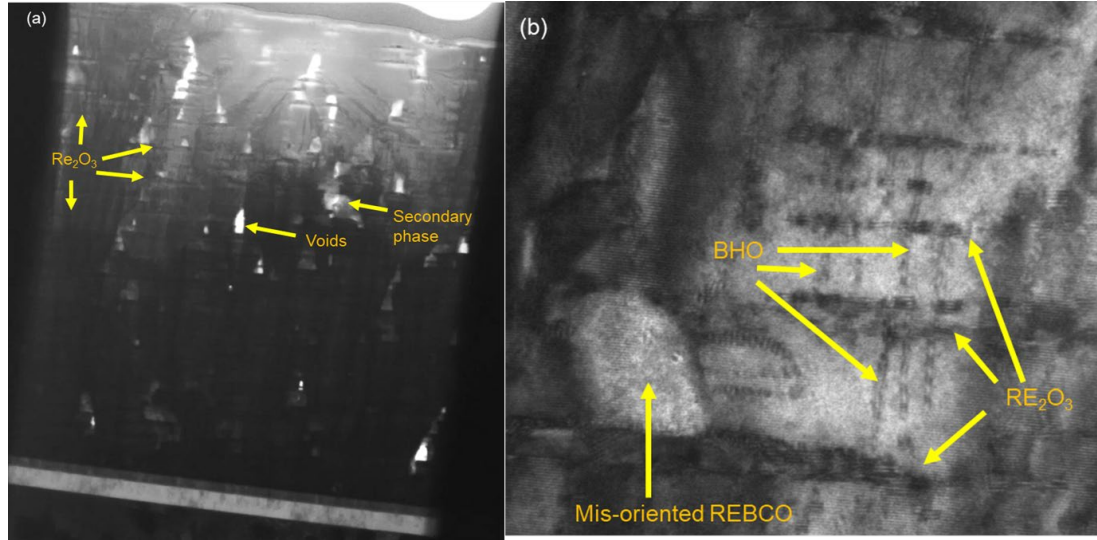


Figure 3-22. (a) shows a whole cross-section TEM microstructure of 5% Hf-A film with (Ba-Hf)/Cu $\sim$ 0.67. (b) shows a magnified image of the middle portion of the cross-section.

3.2.2.2.2. Comparison of the texture of Zr-doped and Hf-doped (Gd, Y)BCO films.

As presented in Figure 3-23, 5% Hf-doped samples show comparatively better in-plane and out-of-plane texture when compared with 5% Zr-doped films. 5% Hf-A and 5% Hf-B films show consistent and better in-plane texture $\sim 2.6^\circ$ (FWHM) and out-of-plane texture of $\sim 0.9^\circ$ (FWHM), independent of the (Ba-Hf)/Cu ratio compared with 5% Zr-A films with in-plane texture $\sim 3.1^\circ$ (FWHM) and out-of-plane texture $\sim 1.1^\circ$ (FWHM). The texture follows the same trend as the c -lattice constant shown in Figure 3-20. This improvement may be due to the reduced strain from the discontinuous nanorods. A better texture certainly improves the current carrying properties of the (Gd, Y)BCO films.

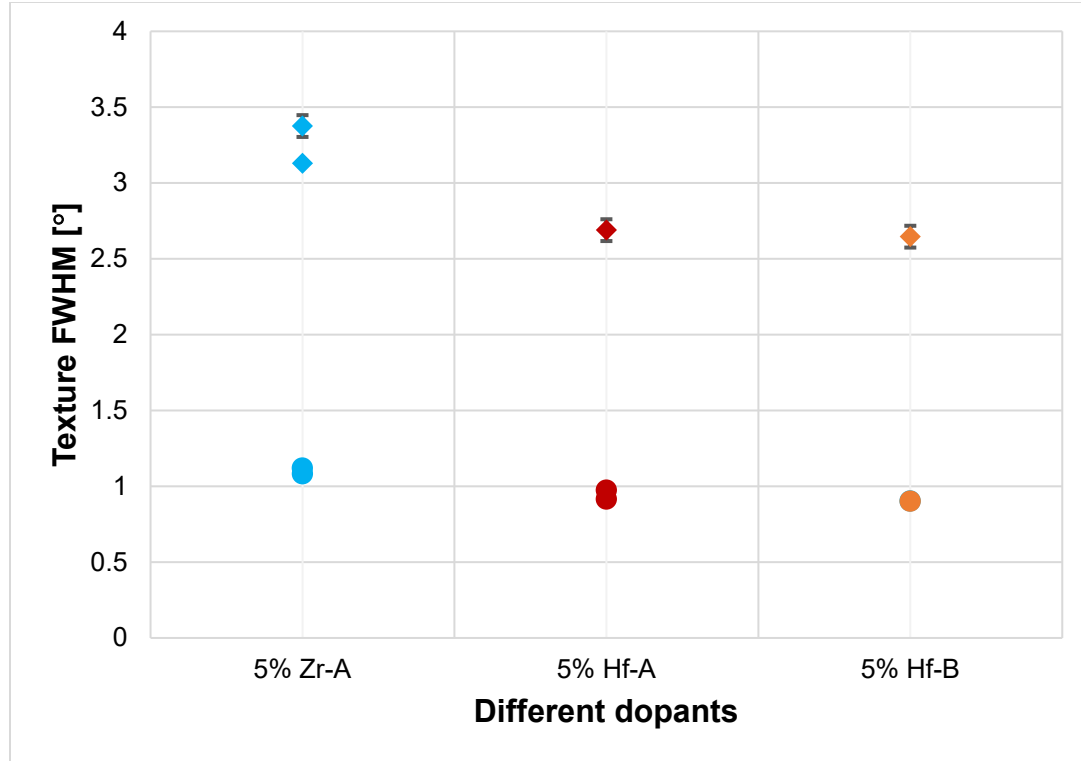


Figure 3-23. Out-of-plane texture and in-plane texture [shown in (FWHM)] from (Gd, Y)BCO(005) ω -scans and (Gd, Y)BCO(103) ϕ -scans respectively of 5% Zr-A, 5 % Hf-A and 5 % Hf-B.

3.2.2.2.3. The effect of 5 mol% Hf (different Ba) on the in-field transport critical current at 65 K

The angular dependence of critical current density (J_c) at 65 K in a 1.5 T magnetic field of 5% Hf-A film (4.7 μm) and 5% Hf-B (film (4.34 μm) is shown in Figure 3-24. For 5% Hf-A film (4.7 μm), J_c at 65 K, 1.5 T ($B \parallel c$ -axis) is $\sim 3 \text{ MA/cm}^2$ (I_c - 1420 A/cm) which is same as that of 5% Zr-A type films, as shown in Figure 3-15. However, minimum J_c of 5% Hf-A film is $\sim$ three-fold higher with an absolute value of 1.1 MA/cm^2 (I_c - 538 A/cm) than 5% Zr-A film. This increase in minimum J_c is attributed to the improvement in self-field J_c of Hf-doped samples. Increased minimum J_c reduces the anisotropy ratio (max.

J_c /min. J_c) from 7.9 for 5% Zr-A film to ~ 2.7 for 5% Hf-A film, making Hf-doped samples more isotropic.

With an increase in Ba in 5% Hf-B film ($4.34 \mu\text{m}$), the whole angular dependence curve shown in Figure 3-24 shifts to a lower value as a result of the reduction in self-field J_c . J_c at 65 K, 1.5 T ($B \parallel c$ -axis) of 5% Hf-B film reduces slightly to 2.55 MA/cm^2 ($I_c - 1110 \text{ A/cm}$) and min. J_c at 65 K, 1.5 T to 0.9 MA/cm^2 ($I_c - 380 \text{ A/cm}$), which is still two-fold higher than that of the 5% Zr-A film. The anisotropy ratio remains similar to that of the lower Ba 5% Hf-A film with an absolute value of 2.8.

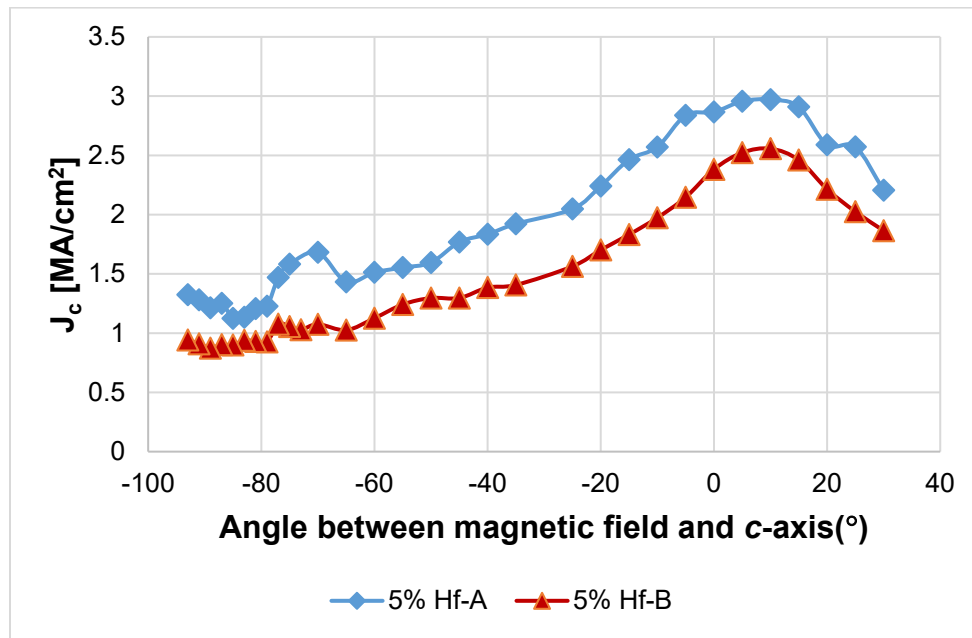


Figure 3-24. Angular dependence of critical current density (J_c) of 5% Zr-A ($\sim 4.35 \mu\text{m}$), 5% Hf-A ($4.7 \mu\text{m}$) and 5% Hf-B ($4.34 \mu\text{m}$) at 65 K in 1.5 T magnetic field.

For applications such as power transmission cables and transformers 0.25 T magnetic field is important. Figure 3-25 shows the angular dependence of 5% Zr-A film ($\sim 4.35 \mu\text{m}$), 5% Hf-A film ($4.7 \mu\text{m}$) and 5% Hf-B film ($4.34 \mu\text{m}$) at 65 K in 0.25 T magnetic field. In general, 5 mol% Hf-doped samples are more isotropic compared with the 5 mol% Zr-doped (Gd, Y)BCO ones. 5% Zr-A film shows a maximum J_c of 3.4 MA/cm^2 ($I_c \sim 1394$

A/cm) near B $\parallel$ *c*-axis with a minimum J_c of 1.37 MA/cm² ($I_c \sim 597$ A/cm) leading to an anisotropy ratio of 2.5. This high maximum J_c at B $\parallel$ *c*-axis for 5% Zr-A film is due to continuous nanorods along the whole thickness of the films, as shown in Figure 3-11(a) and (b), with fewer RE₂O₃ precipitates. 5% Hf-B film (4.34 μ m) show a similar maximum J_c of 3 MA/cm² ($I_c \sim 1487$ A/cm) and a much higher minimum J_c of 2.7 MA/cm² ($I_c \sim 1186$ A/cm) leading to a much lower anisotropy ratio of 1.25. Less anisotropy in 5 mol% Hf-doped films can be attributed to the non-continuous BHO nanorods and high amounts of Re₂O₃ precipitates. Similarly, for . 5% Hf-B film (4.7 μ m) shows a similar higher maximum J_c of 4.8 MA/cm² ($I_c \sim 2311$ A/cm) and a much higher minimum J_c of 3.6 MA/cm² ($I_c \sim 1742$ A/cm) leading to an anisotropy ratio of 1.3. The minimum I_c of 1742 A/cm at 65 K, 0.25 T for . 5% Hf-B film (4.7 μ m) meets our second project milestone of achieving over 1440 A/cm in minimum I_c at 65 K, 0.25 T.

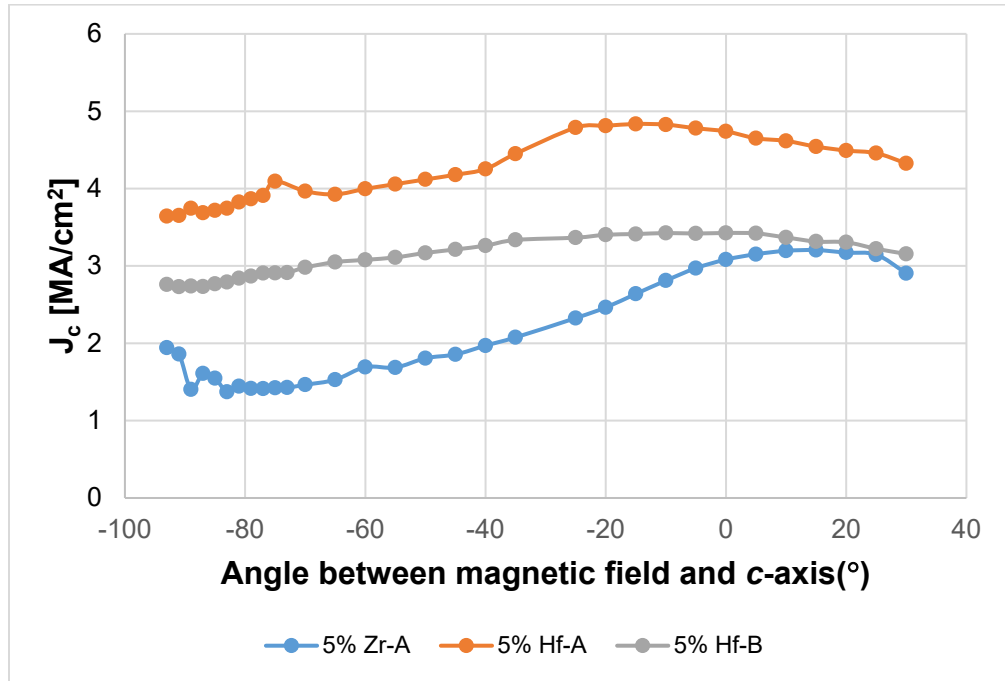


Figure 3-25. Angular dependence of critical current density (J_c) of 5% Zr-A (~ 4.35 μ m), 5 % Hf-A (4.7 μ m) and 5 % Hf-B (4.34 μ m) at 65 K in a 0.25 T magnetic field.

Table 3-7 summarizes the minimum J_c , maximum J_c , and anisotropy ratio at 65 K, 0.25 T and 1.5 T for 5% Zr-A, 5% Hf-A and 5% Hf-B films. It is clearly evident that Hf doping at lower concentrations with less Ba (5% Hf-A film) reduces the anisotropy by a big margin at 1.5 T and 0.25 T. With 5% Hf-A film (4.7 μm) with (Ba-Hf)/Cu ~ 0.67 , we are able to achieve both of our milestones of 1440 A/cm at 65 K, 1.5 T (B $\parallel$ c-axis) and minimum I_c of 1440 A/cm 65 K, 0.25 T.

Table 3-7. Comparison of minimum J_c , maximum J_c and anisotropy ratio at 65 K, 0.25 and 1.5 T for 5% Zr-A, 5% Hf-A and 5% Hf-B films.

	65 K, 1.5 T			65 K, 0.25 T		
	Min. J_c (MA/cm ²)	Max. J_c (MA/cm ²)	Anisotropy ratio	Min. J_c (MA/cm ²)	Max. J_c (MA/cm ²)	Anisotropy ratio
5% Zr-A	0.44	3.24	7.35	1.37	3.20	2.34
5% Hf-A	1.12	2.97	2.64	3.64	4.83	1.33
5% Hf-B	0.87	2.55	2.93	2.73	3.42	1.25

The next discussion is on how improving anisotropy with Hf dopant impacted the J_c at higher field and metrics like lift factor and retention factor, as mentioned in Section 3.2.1.3.

Shown in Table 3-8 is the transport J_c at 77 K, 0T; 65 K, 0 T, 1.5 T and 9 T (B $\parallel$ c-axis) and the lift factor at 65 K, 1.5 and 9 T (B $\parallel$ c-axis) for the 5% Hf-A film (4.78 μm) and 5% Hf-B film (4.34 μm). As previously discussed, both Hf-doped films show much higher self-field J_c values at 77 K and 65 K compared with 5 mol% Zr-doped and 15 mol% Zr-doped films, as shown in Table 3-3. These self-field J_c values are very comparable to those of undoped (Gd, Y)BCO films, as shown in Table 3-3. However, at higher fields of 9 T (B $\parallel$ c-axis), 5% Hf-A and 5% Hf-B films show a J_c of 0.37 and 0.41 MA/cm² respectively which are lower than the 0.5 MA/cm² of 5 mol% Zr-doped films and almost half of the 15 mol% Zr-doped (Gd, Y)BCO films. The reason for this is the reduced lift

factor, while 5 mol% Zr-doped (Gd, Y)BCO and 15 mol% Zr-doped (Gd, Y)BCO films show lift factors of 0.38 and 1.45 respectively at 65 K, 9 T while 5 mol% Hf-doped films show lower lift factors (0.16 -0.21). The reduction in lift factor ($B \parallel c$ -axis) is attributed to the breaking of BHO nanorods with a higher density of in-plane precipitates (e.g., RE_2O_3). Also, the retention factors of these 5 mol% Hf-doped films are 0.58 and 0.06-0.09 at 65 K, 1.5 T and 9 T, which is half of that of 5 mol% Zr-doped (Gd, Y)BCO films with continuous nanorods. From this it can be concluded that by reducing the anisotropy at lower fields at 65 K, the retention factor of the films and the critical current at higher fields are reduced; this reflects the tradeoff between retention factor and anisotropy.

Table 3-8. Comparison of transport J_c at 77 K, 0T; 65 K, 0 T, 1.5 T and 9 T ($B \parallel c$ -axis) and lift factor at 65 K, 1.5 and 9 T ($B \parallel c$ -axis) for a 5% Hf-A film (4.78 μm) and 5% Hf-B film (4.34 μm).

	Transport J_c [MA/cm ²]				Transport Lift Factor	
	77 K, 0 T	65 K, 0 T	65 K, 1.5 T ($B \parallel c$ -axis)	65 K, 9 T ($B \parallel c$ -axis)	65 K, 1.5 T ($B \parallel c$ -axis)	65 K, 9 T ($B \parallel c$ -axis)
5% Hf-A	2.37	5.38	3.13	0.37	1.32	0.16
5% Hf-B	1.95	4.40	2.56	0.41	1.31	0.21

3.2.2.3. The effect of rare-earth content on the microstructural and transport properties of 5 mol% doped (Hf and Zr) thick (Gd, Y)Ba₂Cu₃O_{7- δ}

As described in Section 3.2.2.2., a certain increase in the RE_2O_3 precipitates was observed with Hf doping of (Gd, Y)BCO films, which contributed to reducing the anisotropy at higher temperatures and lower fields. Given these results, it is important to further investigate the effect of RE_2O_3 by intentionally increasing its content in the precursor and observing the effect on anisotropy at the lower fields of 0.25 T and 1.5 T at 65 K.

Two different dopants (Hf and Zr) were studied with two different rare-earth compositional ratios ($Y+Gd = 1.3$ and 1.5). Following are the precursor compositional ratios used in this study with their short forms for easy readability:

5% Zr-A – 5 mol% Zr-doped (Gd, Y)BCO films with precursor compositional ratio of $Y_{0.65}Gd_{0.65}Ba_2Cu_{2.60}Zr_{0.05}$.

5% Zr-AR – 5 mol% Zr-doped (Gd, Y)BCO films with precursor compositional ratio of $Y_{0.75}Gd_{0.75}Ba_2Cu_{2.60}Zr_{0.05}$.

5% Hf-B - 5 mol% Hf-doped (Gd, Y)BCO films with precursor compositional ratio of $Y_{0.65}Gd_{0.65}Ba_{1.92}Cu_{2.60}Hf_{0.05}$.

5% Hf-BR - 5 mol% Hf-doped (Gd, Y)BCO films with precursor compositional ratio of $Y_{0.75}Gd_{0.75}Ba_{1.92}Cu_{2.60}Hf_{0.05}$.

All precursor are prepared at 0.025 M.

3.2.2.3.1. The effect of rare-earth on self-field critical current density at 77 K, 0 T

Figure 3-26 shows a comparison of transport self-field J_c at 77 K for a 5% Zr-A film, a 5% Zr-AR film, a 5% Hf-B film, and two 5% Hf-BR films. All films are over 4 μm thick and prepared with 0.025 M precursors. With increasing the rare-earth content from ($Y+Gd = 1.30$) to ($Y+Gd = 1.50$) for both the Zr and Hf dopants, an increase in self-field J_c of 30-40% was observed. This can be attributed to the increase in Re_2O_3 precipitates with increasing rare-earth content, which helps to increase the self-field J_c , independent of the dopant used.

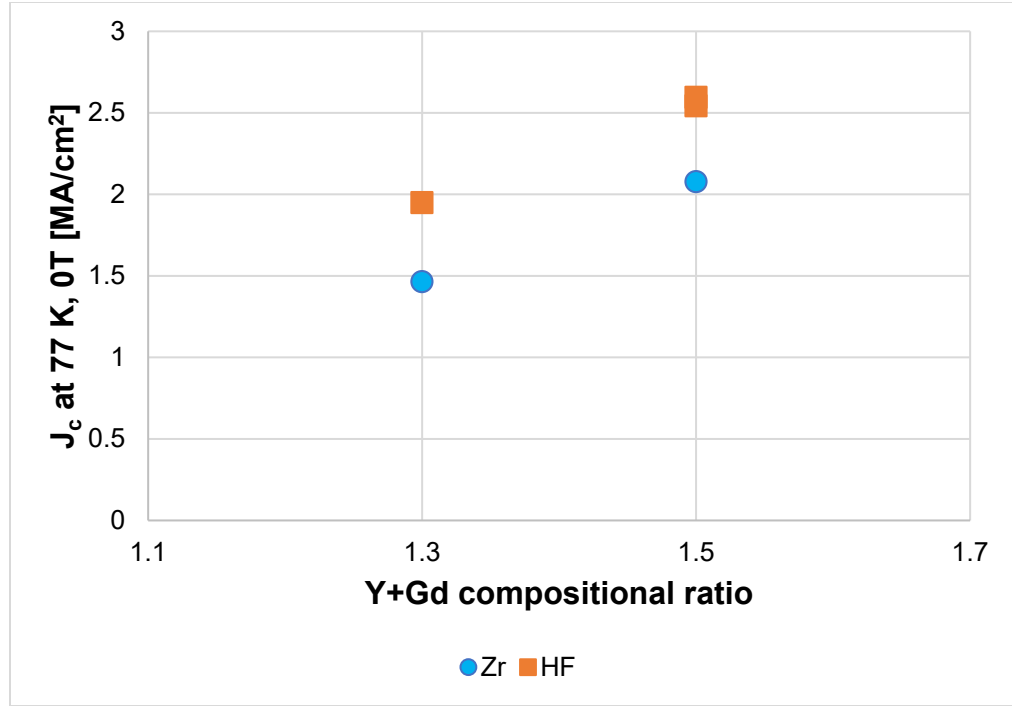


Figure 3-26. Transport J_c at 77 K, 0 T of a 5% Zr-A film, a 5% Zr-AR film, a 5% Hf-B film and two 5% Hf-BR.

3.2.2.3.2 The effect of rare-earth on c -axis lattice constant and composition

Figure 3-27 depicts the c -axis lattice constant of (Gd, Y)BCO determined from the (00 l) peaks by a least-squares fit to the Nelson-Riley function. Eight different samples were analyzed, four doped with 5 mol% Zr and four with 5 mol% Hf. The 5% Zr-A films show consistent c -axis lattice constants of 11.734 Å and 11.737 Å while 5% Zr-AR films with higher Y+Gd of 1.5 increases the c -axis lattice constant to 11.745 Å and 11.75 Å. This increase in c -lattice constant is associated with the large increase in RE₂O₃ precipitate formation [86]. RE₂O₃ has less lattice mismatches with the (Gd, Y)BCO phase because of the inappreciable difference in the c -lattice constant of (Gd, Y)BCO; however, high amounts of RE₂O₃ can induce lattice strain by causing distortions or misfit dislocations that contribute to appreciable increases in the c -lattice constant and deteriorate the crystallinity

of the films. 5 mol% Hf-doped films follow the same trend with increasing rare-earth content as 5 mol% Zr-doped films. 5% Hf-B films show c -axis lattice constants of ~ 11.72 Å, while 5% Hf-BR shows higher c -axis lattice constants of 11.726 Å and 11.739 Å. The reason for 5% Hf-B films having a lower c -lattice constant than the 5% Zr-A film is mentioned in Section 3.2.2.2.1. in detail. Briefly, in 5% Hf-B films, RE_2O_3 increases in density, which breaks nanorods, causing less strain in the films and lowering the c -lattice constant.

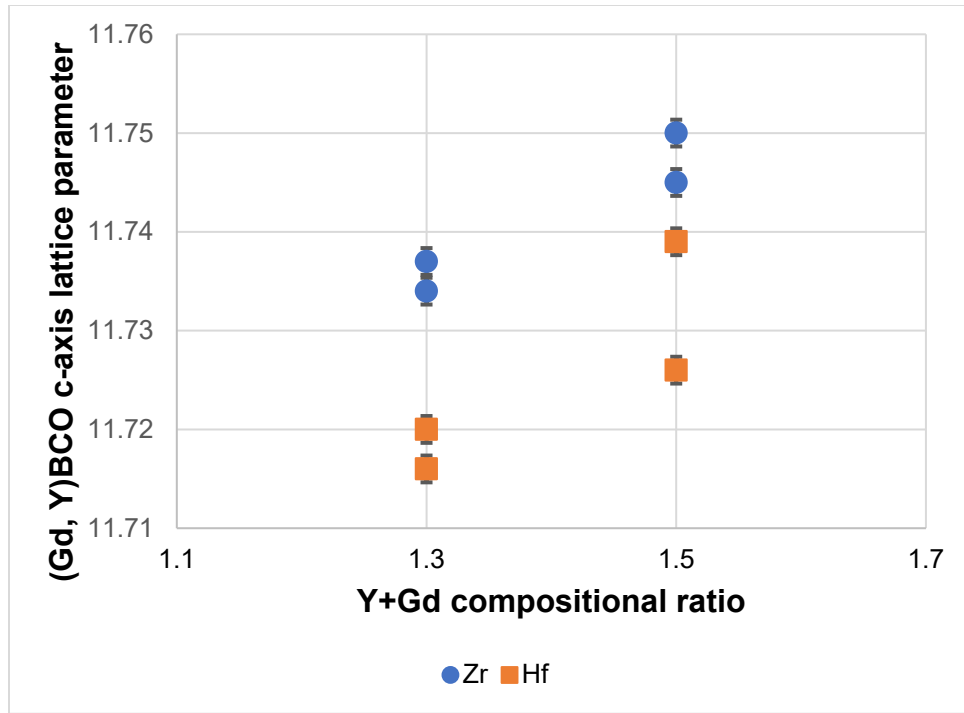


Figure 3-27. c -lattice parameter of two each for 5% Zr-A, 5% Zr-AR, 5% Hf-B and 5% Hf-BR films. All films are over 4 μm thick and prepared with 0.025 M precursors.

3.2.2.3.3. The effect of rare-earth on texture

Figure 3-28 depicts the out-of-plane texture of eight different films, two each for 5% Zr-A, 5% Zr-AR, 5% Hf-B and 5% Hf-BR films. The out-of-plane texture was calculated using an XRD ω -scan of the (Gd, Y)BCO (005) peak. 5% Zr-A films show

reproducible out-of-plane textures of $\sim 1.1^\circ$. However, when the Y+Gd compositional ratio increased to 1.5 in case of 5% Zr-AR films, the out-of-plane texture increases to 1.23° and 1.27° . This increase in out-of-plane texture is due to the deterioration of the crystallinity caused by big increase in in-planar defects such as RE_2O_3 , which increases strain in the (Gd, Y)BCO matrix that can increase the grain boundary misorientation angle. Out-of-plane texture follows the same trend seen in the c -lattice constant, as shown in Figure 3-27.

5% Hf-B films show improved and repeatable out-of-plane textures $\sim 0.9^\circ$. The reason for the better out-of-plane texture is likely the smaller c -lattice constant in Hf-doped samples, as mentioned in Section 3.2.2.2.2. Hf also follows the same trend as Zr; when the Y+Gd compositional ratio increased from 1.3 to 1.5, the out-of-plane texture in case of 5%Hf-BR films increases to 1.24° and 1.21° for the two different samples. The plot in Figure 3-28 reflects the reproducibility of the films generated using A-MOCVD and how different dopants exhibit similar values.

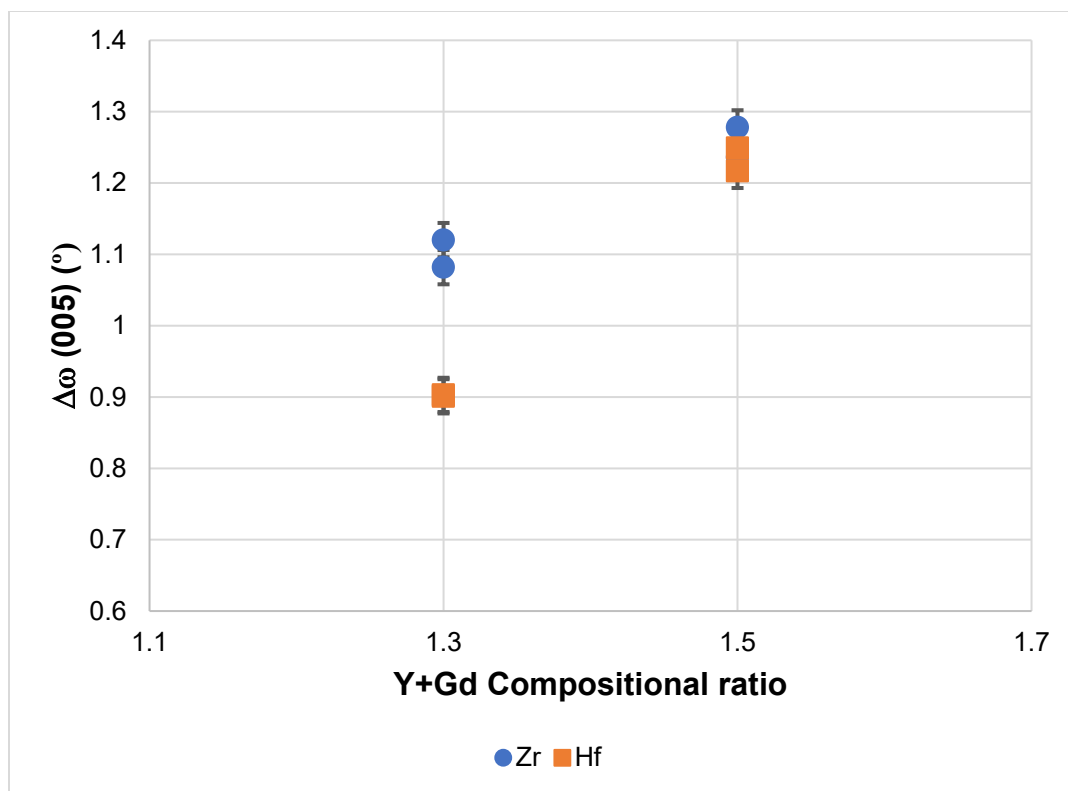


Figure 3-28. Out-of-plane texture [shown in (FWHM)] from (Gd, Y)BCO(005) ω -scans two each for 5% Zr-A, 5% Zr-AR, 5% Hf-B and 5% Hf-BR films.

Figure 3-29 shows the in-plane texture of five different films, three doped with 5 mol% Zr and two doped with 5 mol% Hf. The in-plane texture was investigated by XRD ϕ -scan of the (Gd, Y)BCO (103) peak. Two different 5% Zr-A films show good, repeatable in-plane textures of 3.1° and 3.4°. When the Y+Gd compositional ratio increased to 1.5, the in-plane texture increased to 3.6°. This trend is similar to that observed in the change in out-of-plane texture with increasing rare-earth content. 5 mol% Hf-doped films also follow the same trend as the Zr-doped samples but with a lower value at the lower Y+Gd compositional ratio of 1.3. The in-plane texture of 5% Hf-doped films increases from 2.6° to 3.6° for Y+Gd compositional ratios of 1.3 and 1.5 respectively. This increase in out-of-plane and in-plane texture with increasing rare-earth content is consistent independent of the dopant used. In general, out-of-plane and in-plane texture follow the same trend as the

c -lattice constant, which indicates a strong relationship between them. An increase in the lattice constant disturbs the crystallinity of the films and induces positive strain in the films, which results in coarsening of the grains and grains boundaries, indicating higher in-plane and out-of-plane texture.

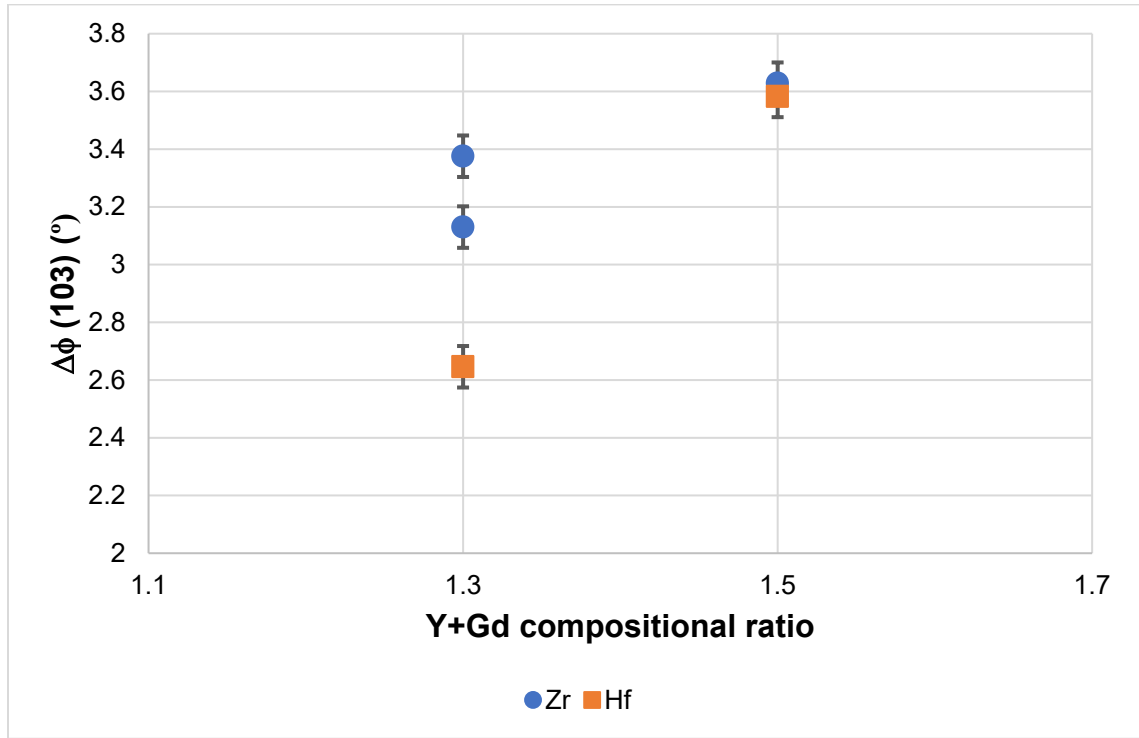


Figure 3-29. In-plane texture (shown in FWHM) from (Gd, Y)BCO(103) ϕ -scans, of a 5% Zr-A film, two 5% Zr-AR films, one 5% Hf-B film and one 5% Hf-BR film.

3.2.2.3.4. The effect of rare-earth on in-field critical current

Figure 3-30. shows angular dependence of critical current density at 65 K, 1.5 T of a 5% Zr-A film, a 5% Zr-AR films, a 5% Hf-B film and a 5% Hf-BR film . All films show higher peaks at the $B \parallel c$ -axis compared with $B \perp c$ -axis indicating more dominating pinning in the c -direction, which can be attributed to the columnar form of BMO (M = Zr or Hf) formed in the c -axis direction of (Gd, Y)BCO. The 5% Zr-A film shows the highest J_c of 3.2 MA/cm² ($I_c = 1408$ A/cm) at the $B \parallel c$ -axis, lowest minimum J_c of 0.44 MA/cm²

($J_c = 192$ A/cm), and lowest J_c peak of ~ 0.44 MA/cm² ($J_c = 287$ A/cm) at the $B \perp c$ -axis at 65 K, 1.5 T. This indicates a very high anisotropy ratio of ~ 8 , showing strong pinning of vortices in the c -axis direction of (Gd, Y)BCO and weak pinning at all other angular orientations. This provides information about the different types of defects occurring in the film's microstructure. Strong pinning in the c -axis direction is related to high-density BaZrO₃ nanocolumns growing continuously over the whole thickness along the c -axis of (Gd, Y)BCO, as shown in Figure 3-11(a) and (b). These continuous nanocolumns pin the vortices very effectively when the field is applied along the c -axis of (Gd, Y)BCO. These nanorods, if not continuous, will not work as effectively. The lowest minimum J_c at 65 K, 1.5 T for this same sample indicates very weak pinning along the a - b plane and its nearby orientations. This is attributed to the lack of in-plane and random defects, which improves pinning at $B \parallel a$ - b and other random orientations. Also, BaZrO₃ nanocolumns' continuous growth is possible because of the lack of in-plane defects, which, if in excess, can break BaZrO₃ nanocolumns' growth along the c -axis of (Gd, Y)BCO and deplete its performance in that direction. When the Y+Gd compositional ratio increases from 1.3 to 1.5, the minimum J_c of 5% Zr-AR film increases by more than two-fold to ~ 1.12 MA/cm² ($J_c = 446$ A/cm) while the J_c at $B \parallel c$ -axis reduces to 2.3 MA/cm² ($J_c = 991$ A/cm) at 65 K, 1.5 T. Also at $B \perp c$ -axis, a - b peak improves by more than two-fold to ~ 1.4 MA/cm² ($J_c = 600$ A/cm). The angular dependence curve of 5% Zr-A film shows superior J_c values than that of 5% Zr-AR film at all orientations except near the $B \parallel c$ -axis (-5° to $+20^\circ$) where pinning by continuous nanocolumns dominates. However, the peak width at the $B \parallel c$ -axis for 5% Zr-AR film is broader than 5% Zr-A indicating pinning centers at a broader range, pointing out that some vol.% BaZrO₃ is not continuous along the c -axis direction and can assume a

splayed formation instead of being aligned with the c -axis of (Gd, Y)BCO. This is an effect of increased in-plane defects, such as RE_2O_3 (Re = Y and Gd), due to the increase of Y+Gd in the compositional ratio of the precursors, which improves the self-field J_c , improves pinning in the $B \perp c$ -axis and nearby direction. Although the J_c at the $B \parallel c$ -axis decreases, it becomes more isotropic with anisotropy ratio reduced to 2.1 (four-fold reduction), which is an important aspect when considering the application of these materials.

Hf-doped samples also follow the effect of rare-earth as in Zr-doped films. 5% Hf-B film with Y+Gd = 1.30 shows J_c of 2.55 MA/cm² ($I_c = 1110$ A/cm) at 65 K, 1.5 T ($B \parallel c$ -axis), which is lower than that of its Zr-doped counterpart with the same rare-earth ratio. Also, the peak is wider than that of the Zr-doped samples. This indicates some fractions of BHO become discontinuous and are broken by the relatively higher amount of RE_2O_3 precipitates. Except at angles near the c -axis (-5° to 25°), 5% Hf-B sample dominate in pinning, confirming the increase of in-planar and random defects. At the $B \perp c$ -axis, 5% Hf-B film shows J_c of 1 MA/cm² ($I_c = 467$ A/cm) and min. J_c of 0.9 MA/cm² ($I_c = 379$ A/cm). This is around two-fold higher than its Zr-doped counterpart. The anisotropy ratio of this film is 2.9, which is over two-fold better than its Zr-doped (Gd, Y)BCO counterpart. Increasing the Y+Gd compositional ratio to 1.5 for the 5% Hf-BR film improves the self-field J_c , as shown in Figure 3-26. This effect dominates and improves the J_c over the entire angular range, raising the J_c at 65 K, 1.5 T to 2.8 MA/cm² ($I_c = 1235$ A/cm) ($B \parallel c$ -axis) and min. J_c to 1.5 MA/cm² ($I_c = 651$ A/cm) and a-b peak to 2.1 MA/cm² ($I_c = 896$ A/cm). Consequently, the angular dependence curve becomes much more isotropic with anisotropy ratio of 1.9 and the peak at the $B \parallel c$ -axis becomes much wider.

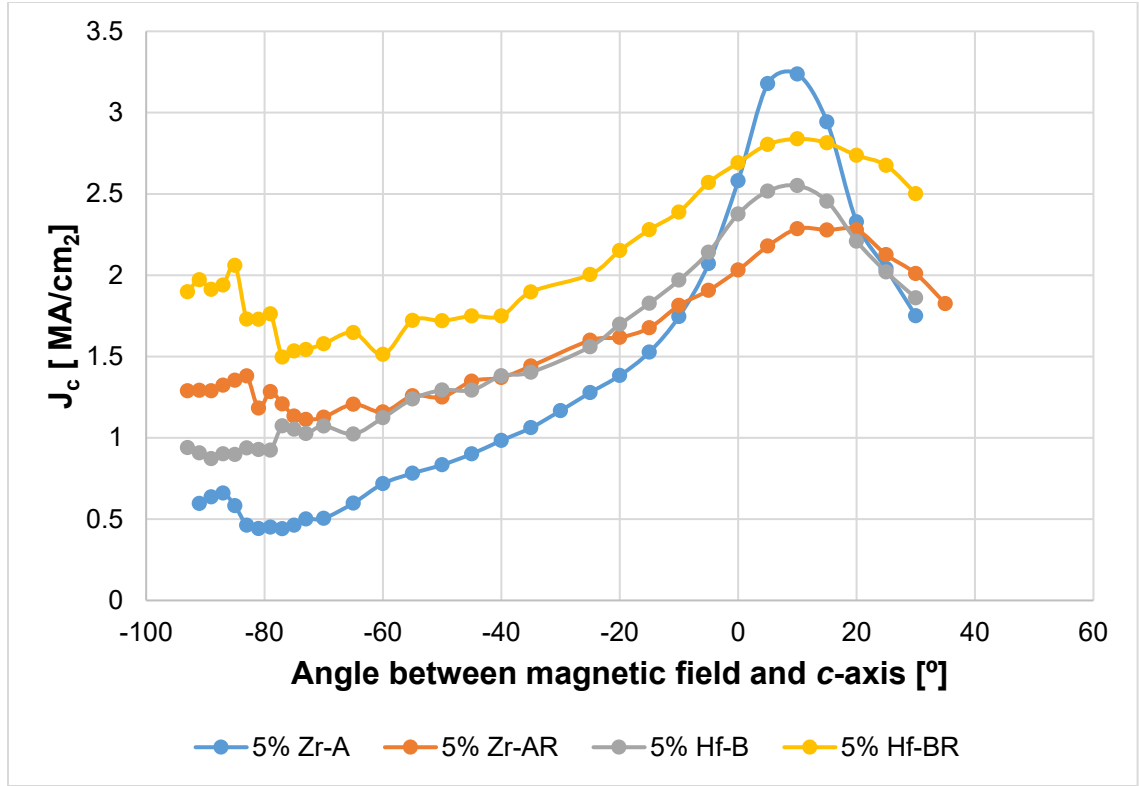


Figure 3-30. Angular dependence of critical current density (J_c) at 65 K, 1.5 T of a 5% Zr-A film, a 5% Zr-AR film, a 5% Hf-B film and a 5% Hf-BR film. All films are at least 4 μm thick and deposited with precursors of 0.025 M.

Shown in Figure 3-31 is the angular dependence of the above four different samples at 65 K, 0.25 T. These follow the same trend with increases in rare-earth as shown in Figure 3-30 for angular dependence at 65 K, 1.5 T. The 5% Zr-A film shows a maximum J_c of 3.2 MA/cm² ($I_c = 1394$ A/cm) and minimum J_c of 1.4 MA/cm² ($I_c = 597$ A/cm), leading to an anisotropy ratio of 2.3. With an increase in rare-earth content to Y+Gd=1.5 for 5% Zr-AR film, anisotropy ratio reduces to 1.1, becoming almost flat with a maximum J_c of 3.5 MA/cm² ($I_c = 1534$ A/cm) and minimum J_c of 3.1 MA/cm² ($I_c = 1349$ A/cm). For the 5% Hf-B film, a maximum J_c of 3.4 MA/cm² ($I_c = 1487$ A/cm) and minimum J_c of 2.7 MA/cm² ($I_c = 1186$ A/cm) were achieved with an anisotropy ratio of 1.3. By increasing the rare-earth content to Y+Gd = 1.5 as in case of 5% Hf-BR film, the maximum J_c increases to 4.8

MA/cm² ($J_c = 2074$ A/cm) and minimum J_c to 4.2 MA/cm² ($J_c = 1846$ A/cm) with an anisotropy ratio of 1.1. Also, with rare-earth content of Y+Gd = 1.3, for both Zr and Hf, J_c is more dominant near and around the $B \parallel c$ -axis indicating the dominance of nanocolumnar defects along the c -axis. It is higher in the Zr-doped samples, due to the presence of continuous BZO nanocolumns along the c -axis. By increasing the rare-earth content to 1.5, J_c seems to dominate near the a - b plane field orientation indicating the dominating presence of in-planar defects compared with nanocolumnar defects in the c -axis direction. The minimum J_c , maximum J_c , and anisotropy ratio at 65 K, 0.25 T and 1.5 T are summarized in Table 3-9.

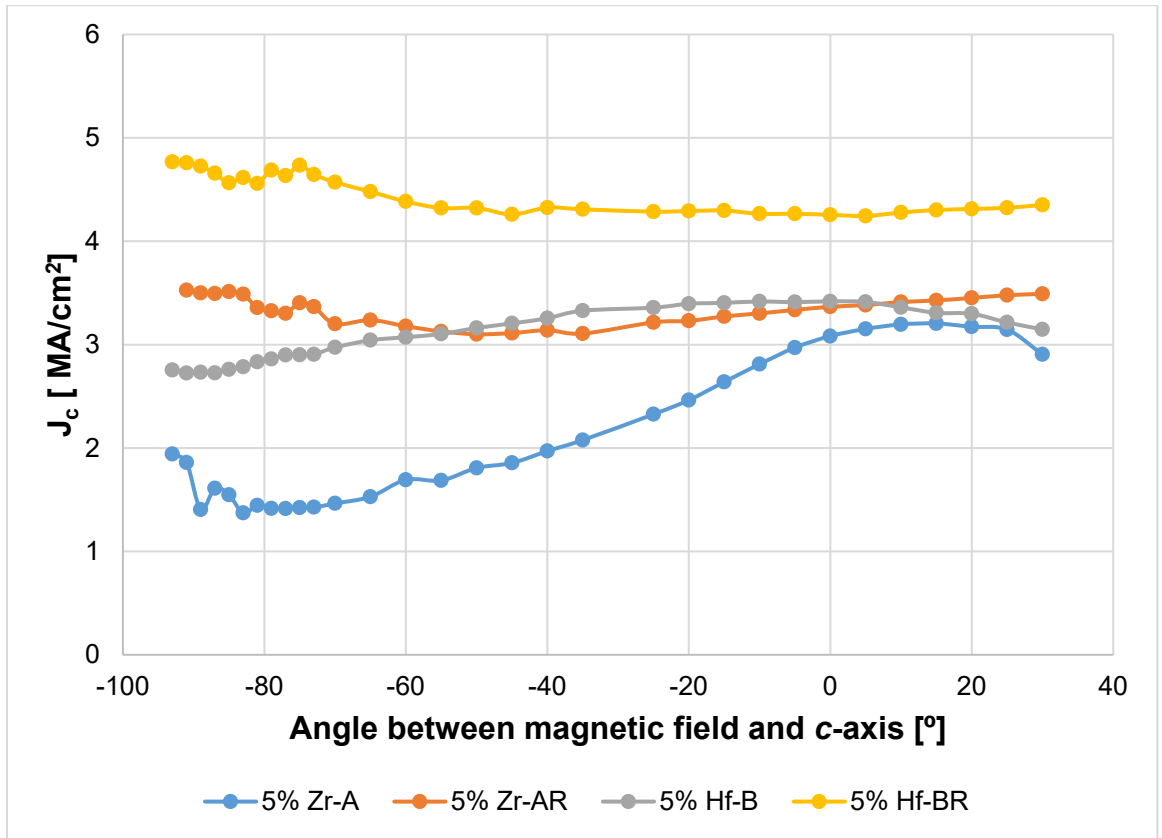


Figure 3-31. Angular dependence of critical current density (J_c) at 65 K, 0.25 T of a 5% Zr-A film, a 5% Zr-AR film, a 5% Hf-B film and a 5% Hf-BR film. All films are at least 4 μ m thick and deposited with precursors of 0.025 M.

Table 3-9. Comparison of transport minimum J_c , maximum J_c and anisotropy ratio at 65 K, 0.25 T and 1.5 T of a 5% Zr-A film, a 5% Zr-AR film, a 5% Hf-B film and a 5% Hf-BR film.

		5% Zr-A	5% Zr-AR	5% Hf-B	5% Hf-BR
		$Y_{0.65}Gd_{0.65}Ba_2Cu_{2.60}Zr_{0.05}$ (4.8 μm)	$Y_{0.75}Gd_{0.75}Ba_2Cu_{2.60}Zr_{0.05}$ (4.3 μm)	$Y_{0.65}Gd_{0.65}Ba_{1.92}Cu_{2.60}Hf_{0.05}$ (4.3 μm)	$Y_{0.75}Gd_{0.75}Ba_{1.92}Cu_{2.60}Hf_{0.05}$ (4.3 μm)
65 K, 0.25 T	Min. J_c (MA/cm ²)	1.4	3.1	2.7	4.2
	Max. J_c (MA/cm ²)	3.2	3.5	3.4	4.8
	Min. I_c (A/cm)	597	1349	1186	1846
	Max. I_c (A/cm)	1394	1534	1487	2074
	Anisotropy (max./min.)	2.3	1.1	1.3	1.1
65 K, 1.5 T	Min. J_c	0.4	1.1	0.9	1.5
	Max. J_c	3.2	2.3	2.6	2.8
	Min. I_c (A/cm)	192	484	379	651
	Max. I_c (A/cm)	1408	994	1110	1235
	Anisotropy (max./min.)	7.4	2.1	2.9	1.9

3.2.3. Summary

This section detailed a descriptive study on optimizing composition for high performance at high temperatures and different magnetic fields for films thicker than 3.5 μm . First, different dopant concentrations were investigated to understand their effects at high temperature and in different fields. It was found that a low dopant concentration (5

mol%) is best suited for high-temperature, low field applications. Three different studies based on the effect of precursor molarity, dopant (e.g., Hf), and higher rare-earth content were performed toward reducing the anisotropy of the films. Considering the results of these studies, the following conclusions can be drawn:

- (1) Undoped (Gd, Y)BCO has the highest self-field J_c at 77 and 65 K and can be used for applications at 77 K and fields lower than 0.2 T.
- (2) 5 mol% Zr-doped (Gd, Y)BCO films provide high critical current along the $B \parallel c$ -axis at 65 K until 5 T with a very high retention factor. This composition was used to achieve our project milestone of 1440 A/cm at 65 K, 1.5 T ($B \parallel c$ -axis), but resulted in a high anisotropy of 8 due to the presence of long and continuous nanocolumns grown along the c -axis. If anisotropy is not critical for the desired application, this composition is optimal.
- (3) 15 mol% Zr-doped (Gd, Y)BCO yielded high critical current at the $B \parallel c$ -axis at 65 K after 5 T with the highest retention factor. At 65 K, 9 T ($B \parallel c$ -axis), it has a $J_c \sim 0.9 \text{ MA/cm}^2$, which is two-fold higher than that of 5 mol% Zr-doped (Gd, Y)BCO. For fields above 5 T, this composition is optimal (if anisotropy is not critical for the desired application).
- (4) Increase in deposition rate (with increase in precursor molarity) doesn't seem to attain the desired goal of lower anisotropy. In contrast, it actually degrades the performance with the increased growth of a -axis-oriented grains caused by the increase in surface roughness with an increased deposition rate.
- (5) Hf dopants at the low concentration of 5 mol% and less Ba (Ba - 1.87 and 1.92) in the compositional ratio tend to form more RE_2O_3 precipitates, which tends

to improve self-field J_c and min. J_c at 65 K, 1.5 T and 0.25 T reducing anisotropy by over two-fold and making it more isotropic. 5% Hf-A film with a precursor compositional ratio of $Y_{0.65}Gd_{0.65}Ba_{1.87}Cu_{2.60}Hf_{0.05}$ was used to reach over 1440 A/cm at 65 K, 1.5 T ($B \parallel c$ -axis) and a minimum I_c of 1740 A/cm at 65 K, 0.25 T, which meets both of our project milestones. For applications at 65 K, at both 0.25 T and 1.5 T, $Y_{0.65}Gd_{0.65}Ba_{1.87}Cu_{2.60}Hf_{0.05}$ is preferable.

(6) Increasing the rare-earth content from (Y+Gd-1.3) to (Y+Gd-1.5) reduces the anisotropy of both Zr-doped as well as Hf-doped (Gd, Y)BCO films. Both Zr-doped and Hf-doped films with Y+Gd-1.5 achieve very low anisotropy ratios of 1.1-1.3 at 65 K, 0.25 T, with Hf-doped films dominating in absolute values. $Y_{0.75}Gd_{0.75}Ba_{1.92}Cu_{2.60}Hf_{0.05}$ films (5% Hf-BR) show a minimum I_c of 1846 A/cm at 65 K, 0.25 T, which is more than 400 A/cm higher than the desired milestone of 1440 A/cm at 65 K, 0.25 T. For applications at 65 K, 0.25 T with low anisotropy and high values, $Y_{0.75}Gd_{0.75}Ba_{1.92}Cu_{2.60}Hf_{0.05}$ is preferable.

3.3. Optimizing composition of thick REBCO ((Gd, Y)BCO) films for low-temperature applications

Due to their high critical temperatures, high irreversibility fields, and high critical current densities, rare earth barium copper oxide (REBCO) coated conductors (CC) have tremendous potential for numerous applications over a range of temperatures (50 K– 4.2 K) and high magnetic fields ranging from 2 to 30 T, such as fusion reactor magnets, high-energy particle accelerators, high-field magnets, magnetic resonance imaging, generators, and motors [57–60,62,64,124]. Several ongoing research and development projects are aimed at developing high-field magnets with insert coils consisting of REBCO due to this material's high current carrying capability in high background fields [125,126]. All of these listed applications would greatly benefit from an increase in power density, which could be achieved by increasing the engineering current density (J_e). Additionally, a significant increase in J_e is perhaps the most direct way of decreasing the cost/performance ratio, which is crucial to achieving widespread utilization of 2G-high temperature superconducting (HTS) in various applications. This is possible by maintaining the same critical current density in thicker films (3.5–5 μm) without any degradation and by modifying the pinning landscape to suit the high-field applications at lower temperatures.

The pinning mechanism at lower temperatures (50–4.2 K) differs significantly from that at high temperatures (77–65 K) due to changes in vortex core size- and temperature fluctuation-associated effects at different temperatures [50,80,109,127–131]. At lower temperatures and high magnetic field regimes, uncorrelated pinning caused by weak point pins and intrinsic pinning has been shown to dominate correlated and random pinning (usually associated with nanocolumns and RE_2O_3 precipitates respectively)

[50,80,109,127–131]. These smaller, but denser weak pins, get depinned at higher temperatures due to high thermal fluctuations and larger vortex sizes, thus causing the strong correlated barium zirconate (BZO) nanorod *c*-axis pinning effects to be quite evident as shown in section 3.2. Although correlated defects, such as nanocolumns, may not have direct strong effects in pinning at lower temperatures, they lead to higher strain, which enhances the formation of weak point pins due to a higher lattice mismatch with the REBCO matrix [50,80,109,127–131]. Hence, it is important to revisit the optimized compositions for high temperature applications and make the appropriate changes in order to optimize the pinning landscape while understanding its effects for achieving high performances at lower temperatures in high magnetic field regimes.

In order to study the effects of different compositions for achieving high performances at low temperatures and high magnetic fields, this study was divided into several sub-sections:

3.3.1 Effects of different dopant concentrations on in-field performance of thick undoped and doped (Gd, Y)BCO at 30 K and 4.2 K.

3.3.2. Effects of different levels of barium concentration on microstructural and electromagnetic properties of 3.8 μm thick, 15 mol% Zr-doped (Gd, Y)BCO films.

3.3.3. Effects of different levels of barium concentration on microstructural and electromagnetic properties of 4.7 μm thick, 15 mol% Hf-doped (Gd, Y)BCO films.

3.3.4. Record-high transport critical current properties achieved in 15 mol% Zr-doped 4+ μm thick (Gd, Y)BCO in low temperature regime (50 –4.2 K).

3.3.1. Effects of different dopant concentrations on in-field performance at 30 and 4.2 K

As shown in section 3.2.1., different dopant concentrations appeared to be suited for different field applications at 65 K. 15 mol% Zr-doped (Gd, Y)BCO films with Ba-Zr/Cu ~ 0.70 demonstrated higher J_c and better retention and lift factors at fields above the 5 T ($B \parallel c$ -axis), when compared with 5 mol% Zr-doped (Gd, Y)BCO with barium (Ba)-Zr/Cu ~ 0.66 , while at fields below 5 T, 5 mol% Zr-doped (Gd, Y)BCO showed a higher J_c . It is important to verify if this behavior changes with a reduction in temperatures when the vortex core size and thermal fluctuations decrease.

3.3.1.1. Effect of dopant concentration on in-field J_c at 30 K

Figure 3-32 represents the magnetic J_c at 30 K in a magnetic field of 0 to 13 T applied perpendicular to the tape of an undoped (Gd, Y)BCO film, a 5 mol% Zr-doped (Gd, Y)BCO film and a 15 mol% Zr-doped (Gd, Y)BCO film. These are the same samples that are shown in figure 3-10 (section 3.2.1.3). As shown in figure 3-32, the self-field J_c at 30 K is the highest for the 5 mol% Zr-doped (Gd, Y)BCO with an absolute value of 12 MA/cm² followed by the 15 mol% Zr-doped (Gd, Y)BCO with a self-field J_c of 9.8 MA/cm², while undoped (Gd, Y)BCO presented the least self-field J_c of 5.3 MA/cm². This is in contrast with the self-field J_c shown at 65 K in figure 3-10 (section 3.2.1.3) in which undoped (Gd, Y)BCO showed the highest self-field J_c . This indicates the effects of strain-induced dense weak pins caused by nanocolumns. Several research groups have proposed a larger effect of weak uncorrelated point pins at temperatures at or below 30 K [50,80,109,127–131]. Also, it has been shown that nanocolumns do not pin as effectively

at lower temperatures (as opposed to higher temperatures), but a higher nanocolumn density increases the strain in the films and creates higher densities of weak pins, which are very effective pinning centers at lower temperatures [50,80,109,127–131]. However, increasing the nanocolumnar density over a certain limit affects the self field J_c adversely by deteriorating the crystallinity of the films and lowering the superconducting volume. This can be seen in 15 mol% Zr-doped (Gd, Y)BCO film in which higher nanocolumn density and hence, denser weak pins are present which improves its in-field properties but its self-field J_c is lower than that of the 5 mol% Zr-doped (Gd, Y)BCO.

The J_c of the undoped (Gd, Y)BCO is consistently lower at all magnetic fields compared with those of 5 and 15 mol% Zr-doped (Gd,Y)BCO. Also, the J_c of the 15 mol% Zr-doped (Gd, Y)BCO film exceeds that of 5 mol% Zr-doped (Gd, Y)BCO at 2.4 T and is dominant at all higher fields. A high J_c of 2.6 MA/ cm² is obtained with 15 mol% Zr-doped (Gd, Y)BCO at 30 K and 13 T ($B \perp$ tape), which is 1.6 times that of the 5 mol% Zr-doped (Gd, Y)BCO ($J_c \sim 1.58$ MA/ cm²) and a 5-times higher J_c than that observed in undoped (Gd Y)BCO ($J_c \sim 0.5$ MA/ cm²). A higher in-field performance of 15 mol% Zr-doped (Gd, Y)BCO validates the reasoning that a high density of weak point pins enhanced pinning at lower temperatures and higher magnetic fields. The higher dopant concentration in 15 mol% Zr-doped films contain a higher density of nanocolumns, which due to greater lattice mismatch with (Gd, Y)BCO matrix induced a higher strain in the film and led to a higher density of weak pins.

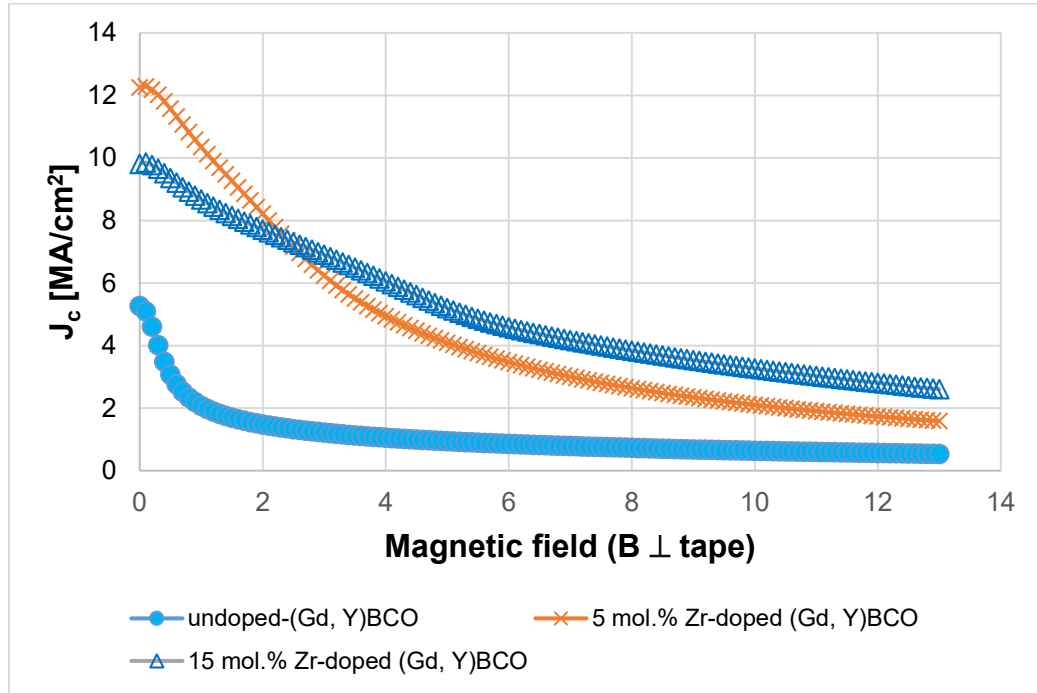


Figure 3-32. Magnetic J_c of an undoped (Gd, Y)BCO film, and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO films at 30 K at magnetic fields of up to 13 T applied perpendicular to the tape.

Table 3-10 depicts the magnetic critical current density (J_c), lift and retention factors at 3 and 13 T along with peak pinning forces (F_p) at 30 K. As shown in table 3-10, increasing dopant concentrations with compensated Ba content caused an increase in nanocolumn densities, which led to better pinning forces, better in-field lift factor, and better retention factors. The lift factor at 30 K and 3 T increases from 1.2 for undoped (Gd, Y)BCO to 7.4 for 5 mol% Zr-doped (Gd, Y)BCO and finally to 15.5 for 15 mol% (Gd, Y)BCO. A similar trend is seen in table 3-10 for the lift factor at 30 K and 13 T. Also, the retention factor is an indication of the rate of decrease of J_c with an increase in the applied magnetic field, representing the pinning strength of available pinning centers for immobilizing vortices. The retention factor increased from 0.2 for undoped (Gd, Y)BCO

to 0.6 for 5 mol% Zr-doped (Gd, Y)BCO and to 1.60 for 15 mol% (Gd, Y)BCO. Also, the F_p increases from 0.07 TN/m³ for undoped (Gd, Y)BCO to 0.21 and 0.32 TN/m³ for 5 and 15 mol% (Gd, Y)BCO, respectively.

Table 3-10. Comparison of the magnetic J_c , retention factor and lift factor at 30 K and 3 and 13 T ($B \perp$ tape) of an undoped, and Zr-doped (Gd, Y)BCO films. Also, the peak pinning force (F_p) of all these films are tabulated.

	J_c [MA/cm ²]		Lift factor		Retention factor		Peak F_p [TN/m ³]
	30 K, 3 T	30 K, 13 T	30 K, 3T	30 K, 13 T	30 K, 3T	30 K, 13 T	30 K
undoped-(Gd, Y)BCO	1.2	0.5	1.19	0.52	0.23	0.10	0.07
5 mol.% Zr-doped (Gd, Y)BCO	6.2	1.6	7.38	1.88	0.60	0.15	0.21
15 mol.% Zr-doped (Gd, Y)BCO	6.9	2.6	15.48	5.84	1.58	0.60	0.34

3.3.1.2. Effects of dopant concentration on in-field J_c at 4.2 K.

Figure 3-33 exhibits the magnetic J_c for the same samples shown in figure 3-32 at 4.2 K at a magnetic field of 0 to 13 T, applied perpendicular to the tape. The trend of J_c for all three different dopant concentrations is similar to that observed in figure 3-32, indicating similar pinning mechanisms at both temperatures. The self-field J_c was highest for the 5 mol% Zr-doped (Gd, Y)BCO with an absolute value of ~ 27 MA/cm², while the self-field J_c for 15 mol% Zr-doped (Gd, Y)BCO was slightly lower (~ 23 MA/cm²). Undoped (Gd, Y)BCO showed 3 times lower self-field J_c of 9.5 MA/cm² compared to the 5 mol% Zr-doped (Gd, Y)BCO and also showed the lowest J_c over whole range of magnetic fields. The cross-over between J_c of 5 mol and 15mol% Zr-doped (Gd, Y)BCO occurred at 2.1 T, which is very similar to the cross-over field of 2.3 T at 30 K.

15 mol% Zr-doped Gd YBCO tends to dominate the 5 mol% Zr-doped (Gd, Y)BCO at all fields above 2 T, indicating dominance of weak pins created by a higher density of nanocolumns with high dopant concentrations. As a result, J_c at 4.2 K and 13 T ($B \perp c$ -axis) is $\sim 7 \text{ MA/cm}^2$ for 15 mol% Zr-doped (Gd, Y)BCO, which is 1.7 times that of the 5 mol% Zr-doped (Gd, Y)BCO of $\sim 4 \text{ MA/cm}^2$ and 4.7 times higher than the J_c ($\sim 1.5 \text{ MA/cm}^2$) of undoped Gd YBCO.

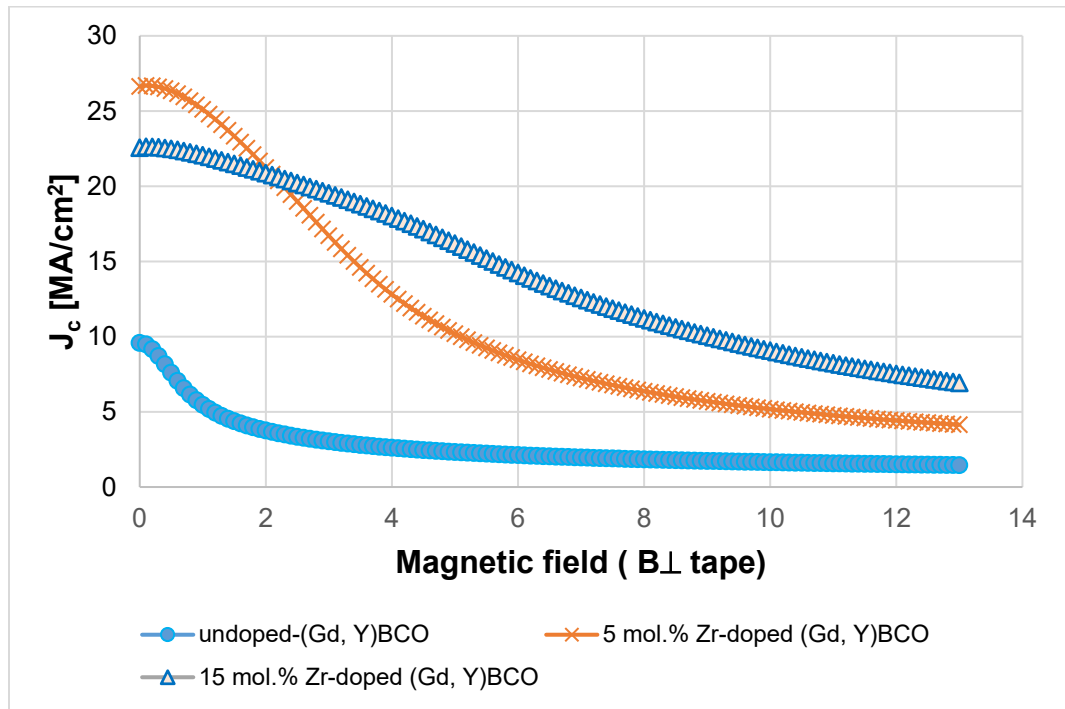


Figure 3-33. Magnetic J_c of an undoped (Gd, Y)BCO film, and Zr-doped (5 mol% and 15 mol%) (Gd, Y)BCO films at 4.2 K under magnetic fields of up to 13 T applied perpendicular to the tape.

Table 3-11 compiles the absolute values of the magnetic J_c , lift and retention factors at 4.2 K, 13 T along with peak pinning force at 4.2 K for undoped (Gd, Y)BCO and 5 and 15 mol% Zr-doped (Gd, Y)BCO films. The trends for retention and lift factors matched very well with the 30 K in-field J_c characteristics. The lift factor increases from 1.42 for

undoped (Gd, Y)BCO to 4.9 for 5 mol% (Gd, Y)BCO and another 3 times higher to 15.5 for 15 mol% (Gd, Y)BCO. The retention factor shows a similar increasing trend from 0.15 for undoped (Gd, Y)BCO to 0.18 for 5 mol% (Gd, Y)BCO to a comparatively high value of 0.69 for 15 mol% (Gd, Y)BCO. The F_p is highest for 15 mol% Zr-doped (Gd, Y)BCO with an absolute value of 0.91 TN/m^3 , which is 68% higher than $F_p \sim 0.54 \text{ TN/m}^3$ of the 5 mol% Zr-doped (Gd,Y)BCO. Undoped (Gd,Y)BCO showed the lowest $F_p \sim 0.19 \text{ TN/m}^3$ as expected.

Table 3-11. Comparisons of magnetic J_c , retention and lift factors at 4.2 K, 13 T ($B \perp$ tape) of an undoped, and Zr-doped (Gd, Y)BCO films. Also, the F_p of all of the above films at 4.2 K are tabulated.

	J_c [MA/cm ²]	Lift factor	Retention factor	Peak F_p [TN/m ³]
	4.2 K, 13 T	4.2 K, 13 T	4.2 K, 13 T	4.2 K
undoped-(Gd, Y)BCO	1.45	1.42	0.15	0.19
5 mol.% Zr-doped (Gd, Y)BCO	4.14	4.90	0.18	0.54
15 mol.% Zr-doped (Gd, Y)BCO	6.92	15.51	0.69	0.91

As seen in the above results, it is clear that the high dopant concentration (15 mol%) is beneficial for improving pinning at low temperature and high-magnetic field conditions as a result of formation of a high density of uncorrelated defects (weak point pins) with strain caused by a higher density of nanocolumns than the defects in 5 mol% films. It was previously reported by our group that by changing Ba concentrations in the (Gd, Y)BCO matrix, there is a possibility of increasing the nanocolumn density by reducing spacing between them [122]. However, all films in that study were 25 mol% Zr-doped (Gd, Y)BCO with a thickness of $\sim 0.9 \mu\text{m}$.

3.3.2. Effects of different levels of barium concentration on microstructural and electromagnetic properties of 3.8 μm thick, 15 mol% Zirconium (Zr)-doped (Gd, Y)BCO films

In this section, the effects of different Ba concentration levels on the microstructural and electromagnetic properties of 15 mol% Zr-doped (Gd, Y)BCO with film thickness $\sim 3.8 \mu\text{m}$ are reported. All the compositional ratios of other elements (Y, Gd, Cu, Zr) in the precursor are kept constant, and only the barium compositional ratio was varied extensively from Ba-2.0 to 2.05, 2.10, 2.15, 2.25, and finally to 2.35.

3.3.2.1. Effects of different Ba levels in the precursor compositional ratio to (Ba-Zr)/Cu in the films

The interpretation of the ratio (Ba-Zr)/Cu is given below:

$$\frac{BaR}{Cu} = \frac{Ba - M}{Cu}$$

in which BaR is the residual Ba in the (Gd, Y)BCO matrix (atomic percentage [at%]), Cu is the Cu-normalized concentration obtained from inductively coupled plasma-mass spectroscopy (ICP-MS) (at%), Ba is the total Ba-normalized concentration obtained from ICP-MS (at%), and M is the normalized dopant (Hf or Zr) concentration obtained from ICP-MS (at%).

Figure 3-34 shows the (Ba-Zr)/Cu of multiple 15 mol% Zr-doped (Gd, Y)BCO films with different Ba compositional ratios ranging from 2.0, 2.05, 2.10, 2.15, 2.25 to 2.35. Ba-, Zr, and Cu-normalized concentrations (at%) are obtained by ICP analysis of each film. Since the dopant concentration (15 mol% Zr) is kept constant for all films, and

there has been no evidence until now of Zr forming any other secondary phase except BaZrO_3 , the increase in $(\text{Ba-Zr})/\text{Cu}$ should indicate an increase of Ba in the REBCO matrix. With an increase in Ba in the precursor, the $(\text{Ba-Zr})/\text{Cu}$ increased, indicating a subsequent increase in Ba in the (Gd, Y)BCO matrix. The ratio of the increase in Ba in the film to that in the precursor is higher until Ba-2.10 after which it reduces, indicating that the conversion rate of barium from precursor to film decreased after Ba-2.10.

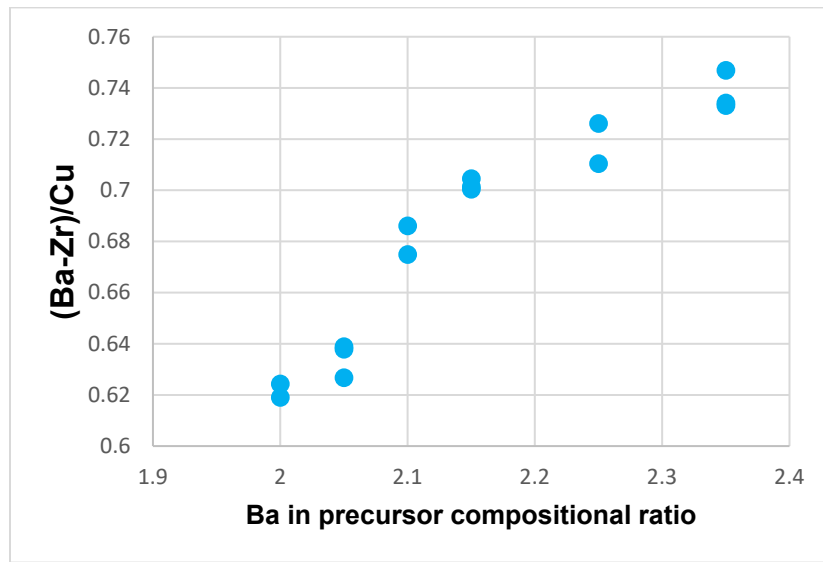


Figure 3-34. $(\text{Ba-Zr})/\text{Cu}$ of multiple 15 mol% Zr-doped (Gd, Y)BCO films with different Ba compositional ratio (2.0, 2.05, 2.10, 2.15, 2.25, and 2.35) in the precursor. All films are $\sim 3.8 \mu\text{m}$ thick and deposited using 0.025 M precursor.

In order to simplify the comparison of different microstructural properties and electromagnetic properties of different Ba films, the average of $(\text{Ba-Zr})/\text{Cu}$ of multiple films with each compositional ratio has been calculated and tabulated in table 3-12.

Table 3-12. Average (Ba-Zr)/Cu of multiple 15 mol% Zr-doped (Gd, Y)BCO films with different Ba compositional ratios (2.0, 2.05, 2.10, 2.15, 2.25, and 2.35) in the precursor.

	Average (Ba-Zr)/Cu
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_2\text{Cu}_{2.60}\text{Zr}_{0.15}$	0.62
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.05}\text{Cu}_{2.60}\text{Zr}_{0.15}$	0.63
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.10}\text{Cu}_{2.60}\text{Zr}_{0.15}$	0.68
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.15}\text{Cu}_{2.60}\text{Zr}_{0.15}$	0.70
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.25}\text{Cu}_{2.60}\text{Zr}_{0.15}$	0.72
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.35}\text{Cu}_{2.60}\text{Zr}_{0.15}$	0.74

3.3.2.2. Effects of different levels of Ba concentration on the self-field J_c of 15 mol% Zr-doped (Gd, Y)BCO at 77 K

Figure 3-35 shows the self-field J_c of 15 mol% Zr-doped (Gd, Y)BCO films with Ba compositional ratios increasing from 2.0 to 2.35 in the precursor while keeping the concentration of all other elements constant.

With increasing Ba in the composition, Ba in the (Gd, Y)BCO matrix starts to increase, and it transitions from a Cu-rich film (Ba-2.00 and Ba-2.05) to a Ba-rich film (Ba-2.10 and above) as shown in table 3-12. In the Cu-rich film, CuO secondary phases forms, which increases the surface roughness leading to the growth of mis-oriented a -axis grains [112,132]. Secondary phases and a -axis-oriented grains can impede current transport along the a -b plane of the film and hence, cause degradation in the self-field J_c . As can be seen in figure 3-35, the 15 mol% Zr-doped (Gd, Y)BCO films with Ba =2.0 and 2.05 compositional ratios shows a lower transport self-field J_c of ~ 0.4 - 0.7 MA/cm^2 . As Ba increases (Ba =2.10) and the film progresses toward the proper stoichiometry (Ba:Cu= 2:3), formation of a -axis oriented grains reduces and hence, transport self-field J_c improves with absolute values between ~ 0.75 and 0.98 MA/cm^2 . Upon further increasing Ba from Ba-2.15 up to 2.35, a sharp and consistent drop in the self-field J_c can be observed. With Ba-

2.15, a 77 K self-field J_c reduces to ~ 0.5 to 0.6 MA/cm² while at Ba-2.25, it further decreases to 0.3 MA/cm². At Ba-2.35, the self-field J_c at 77 K showed the lowest value of ~ 0.15 MA/cm².

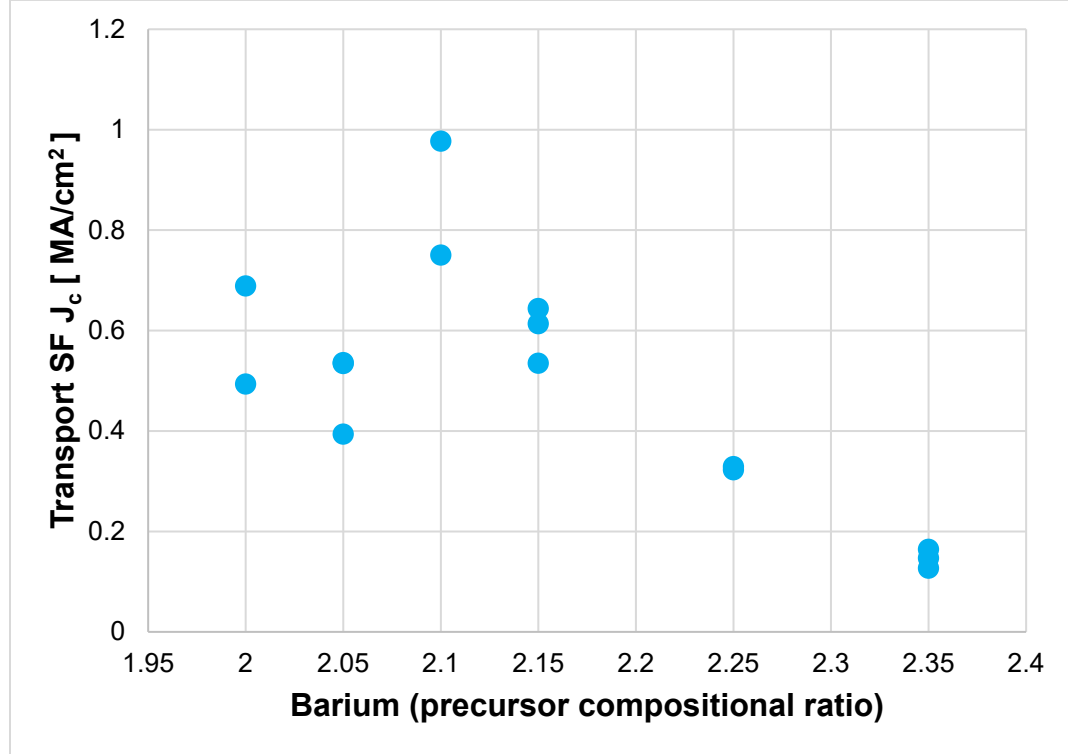


Figure 3-35. Transport J_c at 77 K and 0 T for 15 mol% Zr-doped (Gd, Y)BCO with different Ba compositional ratios of 2.0, 2.05, 2.10, 2.15, 2.25, and 2.35 in the precursor.

In order to verify the decrease of a -axis grains with increasing barium, theta-2theta diffraction patterns of 15 mol% Zr-doped (Gd, Y)BCO films with different Ba compositional ratios of 2.0, 2.05, 2.10, 2.15, 2.25, and 2.35 in the precursor were carried out in the range of 45° to 48° as shown in figure 3-36. The Ba-2.0 film shows a higher (200) peak, indicating the highest amount of a -axis oriented grains that formed due to the Cu-rich film. As the Ba compositional ratio increased to 2.05 and 2.10, the (200) peak

intensity decreases, indicating a reduction in the quantity of these mis-oriented grains. This resonates with the increase in the-77 K self-field J_c with the increase in Ba as shown in figure 3-35. After increasing barium to 2.15 and above, there are no traces of (200) peak, indicating no formation of any a -grains at this Ba concentration. However, the 77 K self-field J_c decreases when Ba increases from 2.10 to 2.15; this self-field J_c decrease is related to the deterioration of texture and increase in c -axis lattice constant, which will be discussed later. Another important feature is the shift of the REBCO (006) peak toward a lower 2 theta value with increasing Ba from 2.0 to 2.15, indicating an increase in the c -axis lattice constant. It is also interesting to note that beyond Ba 2.15, the 2 theta values seem to be independent of increasing Ba in the film.

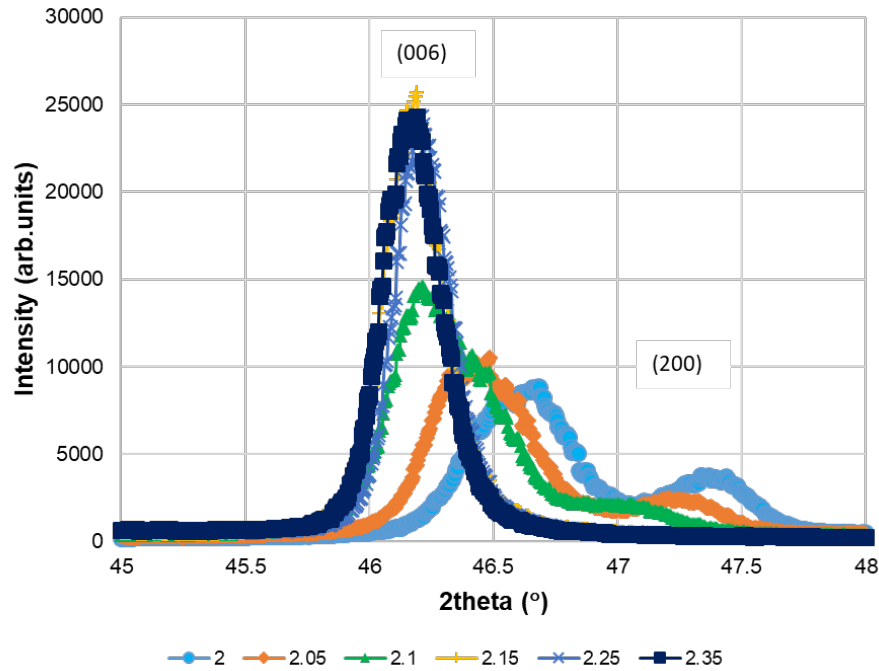


Figure 3-36. X-ray diffraction (XRD) theta-2theta patterns of 15 mol% Zr-doped (Gd, Y)BCO films with different Ba compositional ratios (2.0, 2.05, 2.10, 2.15, 2.25, and 2.35) in the precursor.

3.3.2.3. Effects of different levels of Ba concentration on texture and the *c*-axis lattice constant of 15 mol% Zr-doped (Gd, Y)BCO

Figure 3-37 shows the out-of-plane and in-plane texture values of 15 mol% Zr-doped (Gd, Y)BCO with Ba compositional ratios ranging from 2.0 to 2.35 in the precursor. Out-of-plane and in-plane texture values (shown in degrees of full-width-at-half-maximum [FWHM]) are obtained from (Gd, Y)BCO(005) ω -scans and (Gd, Y)BCO(103) ϕ -scans, respectively.

Out-of-plane texture of the films is in the range of 1.35° to 1.91° for all of the different Ba compositional ratios, indicating no systematic variation with increasing Ba concentration. However, the in-plane texture appears to change with different amounts of Ba. As shown in figure 3-37, in-plane texture values for Ba-2.0, 2.05, and 2.10 are similar in the range of $\sim 4.4^\circ$ to 5.3° , which is at a higher level when compared with that of 5 mol% Zr-doped (Gd, Y)BCO and un-doped (Gd, Y)BCO shown in Table 3-2, section 3.2.1.2. These high in-plane and out-of-plane texture values for Ba-2.0, 2.05, and 2.10 films could be associated with the increase in surface roughness due to the formation of secondary phases and *a*-axis oriented grains. With additional increase in Ba in the compositional ratio to Ba-2.15, 2.25, and 2.35, the in-plane texture deteriorates sharply and increases from respective values of 5.5° to 6.8° and then to 7.5° . The reason for this sharp increase in the in-plane texture with Ba above 2.15 is not clear and still under study. Some of the probable suspects could be formation of a secondary Ba-rich phase or increase in nanocolumns density (this will be examined in later sections), which could cause a deterioration in texture. This increase in the in-plane texture starting at Ba 2.10 could be a reason for the decrease in the 77 K self-field J_c as observed in figure 4.

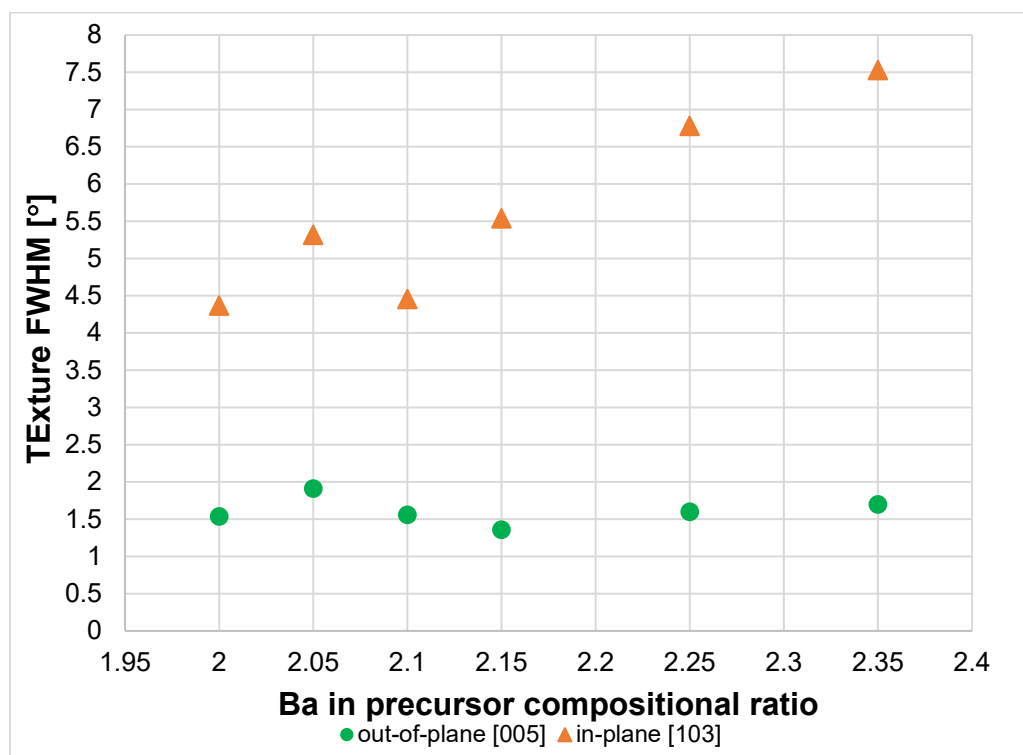


Figure 3-37. Out-of-plane and in-plane texture (shown in FWHM) of 15 mol% Zr-doped (Gd, Y)BCO films with different Ba compositional ratios of 2.0, 2.05, 2.10, 2.15, 2.25, and 2.35 in precursor.

In order to further investigate the effect of Ba on texture and electromagnetic properties, *c*-axis lattice constant of 15 mol% Zr-doped (Gd, Y)BCO films with different amounts of Ba (Ba-2.0 up to 2.35) were calculated from the (00*l*) peaks of (Gd, Y)BCO using a least-squares fit to the Nelson-Riley function [105] as shown in figure 3-38.

A sharp increase in the *c*-axis lattice constant of (Gd, Y)BCO from 11.66 Å for Ba-2.00 to 11.71 Å for Ba-2.05 and further to 11.73–11.742 Å for Ba-2.10 is shown in figure 3-38. Correspondingly, an increase in 77 K self-field *J_c* from Ba-2.00 up to 2.10 occurred as shown in figure 3-35. This contradictory behavior can be explained as follows: with an increase in Ba from 2.0 to 2.10, secondary phase content and *a*-axis-oriented grains reduced

as observed in figure 3-36, which led to an improvement in the self-field J_c . On further increasing Ba to 2.15 and 2.25, a relatively slower increase in the c -axis lattice constant to 11.75 Å and 11.75–11.76 Å can be observed. At the highest Ba concentration of 2.35, the c -axis lattice constant shows a small drop to ~ 11.74–11.75 Å. If cation substitution between Ba and Y is taken into account, which can occur in Ba-rich films [133], an increase in c -axis lattice constant would be expected with Ba entering Y sites. This substitution could cause a degradation in crystallinity and hence, a deterioration in texture. However, instead of an increase, a decrease in the lattice constant has been observed in figure 3-38 when Ba in the compositional ratio increased from 2.25 to 2.35; this finding does not support the cationic substitution argument. Since we can observe an increase in Ba in the film with a corresponding increase in Ba in the precursor (specifically Ba-2.15, 2.25, and 2.35), there is a fair possibility of formation of some Ba-rich secondary phases.

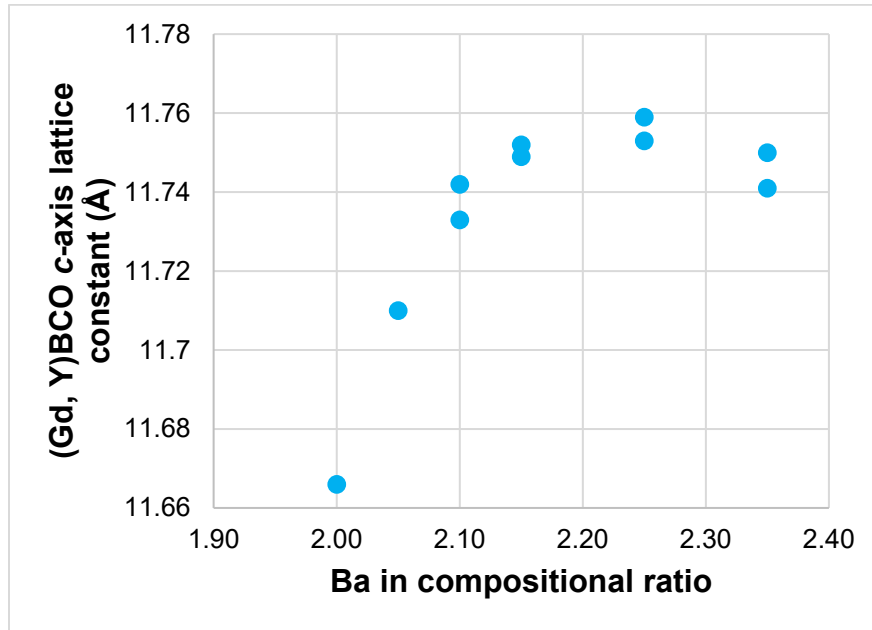


Figure 3-38. The c -lattice parameter of 15 mol% Zr-doped (Gd, Y)BCO with different Ba compositional ratios of 2.0, 2.05, 2.10, 2.15, 2.25, and 2.35 in the precursor.

3.3.2.4. Effects of different levels of Ba concentration on the in-field J_c of 15 mol.% Zr-doped (Gd, Y)BCO at 4.2 K

Figure 3-39 depicts the magnetic J_c at 4.2 K, 13 T ($B \perp$ tape) for the 15 mol% Zr-doped (Gd, Y)BCO with different amounts of Ba ranging from 2.0 to 2.35 in the precursor compositional ratios. A lower in-field $J_c \sim 1$ MA/cm² for Ba-2.0 and 2.05 is due to the formation of a large amount of *a*-axis-oriented grains and secondary phases, such as CuO, which impedes the current and also blocks the growth of continuous nano-columns that affects the in-field pinning properties. Increasing Ba to 2.10 decreases the *a*-axis oriented grains (figure 3-36), leading to the improvement of the self-field J_c (figure 3-35) and also formation of more continuous nanocolumns. Due to the higher lattice mismatch with the (Gd, Y)BCO matrix, these continuous nanocolumns induces higher strain, which leads to the formation of weak pins that dominated pinning at low temperatures, such as 4.2 K [50,80,109,127–131]. As a result, 15 mol% Zr-doped (Gd, Y)BCO with Ba-2.10 shows an improved and consistent in-field J_c of ~ 4 MA/cm². As Ba increases to 2.15, the highest in-field J_c of ~ 7 MA/cm² was achieved. It is important to note that the highest self-field J_c peak was shown with Ba-2.10 in figure 3-35; however, at 4.2 K, 13 T ($B \perp$ tape), 15 mol% Zr-doped (Gd, Y)BCO film with Ba-2.15 shows the highest J_c , indicating that (Gd, Y)BCO film with Ba-2.15 ([Ba-Zr]/Cu ~ 0.70) has better pinning characteristics than any other Ba content. However, as the Ba is increased further to 2.25, J_c drops to ~ 5.7 MA/cm², which is still higher than the J_c of Ba-2.10. A better in-field J_c of Ba-2.25, when compared with Ba-2.10 in spite of the lower 77 K self-field J_c , must be due to the high density of nanocolumns which results in a higher density of weak point pins that are required at 4.2

K for effective immobilization of vortices. Also, the lower in-field J_c of Ba-2.25 when compared with Ba-2.15 could be attributed to its comparatively lower self field J_c due to in-plane texture degradation. Also, no change in the c -axis lattice constant above Ba-2.15 indicates no significant change in the nanocolumn density. At the highest Ba concentration of Ba-2.35 used, a sharp drop in J_c to an absolute value of $\sim 1.90 \text{ MA/cm}^2$ can be seen in figure 3-39.

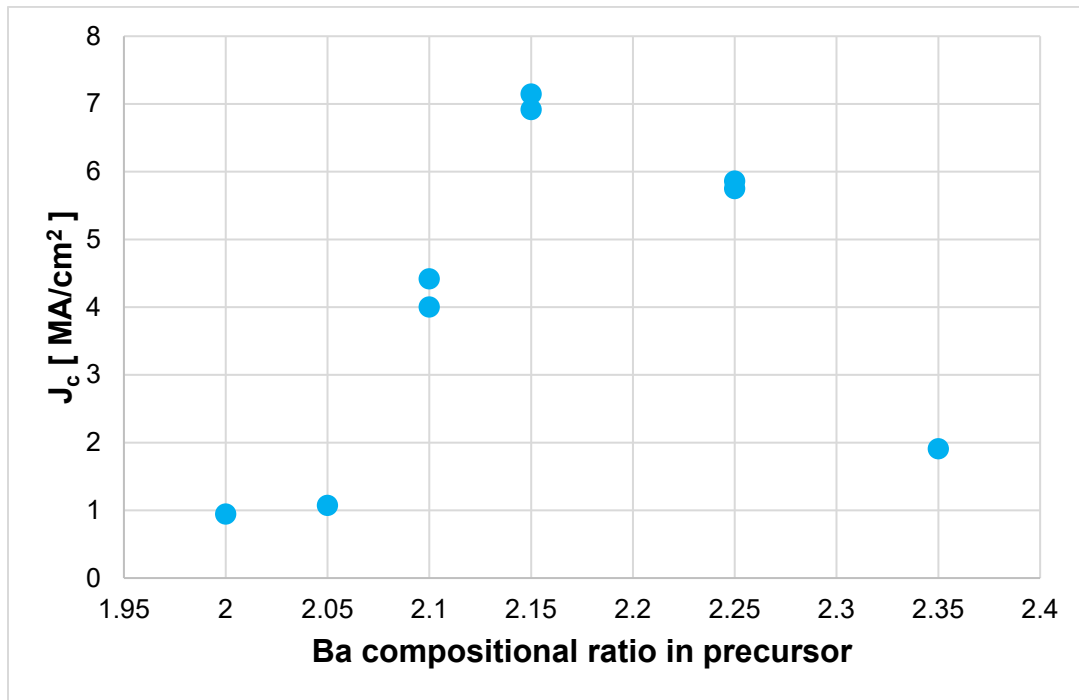


Figure 3-39. Magnetic J_c at 4.2 K, 13 T ($B \perp$ tape) of 15 mol% Zr-doped (Gd, Y)BCO with different Ba compositional ratios (2.0, 2.05, 2.10, 2.15, 2.25, and 2.35) in the precursor.

In order to confirm the hypothesis that with increasing barium from 2.0 till 2.35, BaZrO_3 becomes continuous, and that its density increases from 2.0 to 2.15 and remains constant at higher levels of Ba, plan- and cross-sectional microstructures of three different films (Ba-2.0, 2.15, and 2.35) were analyzed and shown in figure 3-40. Figure 3-40 (a–c)

shows the transmission electron microscopy (TEM) plan-view images, while 3-40 (d–f) represent TEM cross-sectional views of 15 mol% Zr-doped (Gd, Y)BCO with Ba-2.0 (Ba-Zr/Cu~0.62), Ba-2.15 (Ba-Zr/Cu~0.70), and Ba-2.35 (Ba-Zr/Cu~0.74), respectively. Horizontal thin arrows indicates normal BZO while horizontal thick arrows depicts bottle shaped BZO. Vertical arrows are used to indicate RE₂O₃ precipitates or plates. For Ba-2.0, shown in figure 3-40 (d), BaZrO₃ nanocolumns can be observed growing along the *c*-axis of (Gd, Y)BCO as indicated by horizontal thin arrows. These nanocolumns are interrupted by RE₂O₃ plate-like precipitates (indicated by vertical arrows) growing along the *ab* plane. Also, many stacking faults were observed (not shown here) in Ba-2.0 15 mol% Zr-doped (Gd, Y)BCO films. Figure 3-40 (a) represents the plan-view of the same sample, indicating a sparse nanocolumnar density with an average BZO size and spacing of ~ 5.9 and ~ 29.3 nm, respectively. Large spacing between nanocolumns and a low matching field as shown in table 3-13 explain the lower in-field *J_c* for this film as was shown in figure 3-39. As the Ba is increased to 2.15, nanocolumns becomes more continuous along the film, and the spacing between them decreases as shown in figure 3-40 (b) and (e). An interesting feature of the Ba-2.15 film is the change in shape of BaZrO₃ nanocolumns that grew continuously along the film, as discussed in 3.2.1.2. These BaZrO₃ nanocolumns vary in diameter along the thickness of the films, showing bottle-like (larger diameter sections) and normal nanocolumn shapes. The bottle shape is indicated in figure 3-40(e) with a thicker horizontal arrow. Also, there no traces of RE₂O₃ precipitates in figure 3-40(e). The BZO diameter for Ba-2.15, 15 mol% Zr-doped (Gd, Y)BCO film varies between 4 and 14 nm with an average diameter ~ 10 nm. A large drop in BZO spacing can be seen in figure 3-40 (b), which indicates an increase in nanocolumn density and hence a higher matching field. Growth of

continuous BZO nanocolumns and reduction in BZO spacing (~ 17 nm) increases the matching field to ~ 7.2 T for Ba-2.15 as tabulated in table 3-13. As mentioned earlier, high nanocolumn density induces higher strains in the film leading to the formation of more weak point pins, which serves as an effective pinning centers at 4.2 K, since the coherence length at low temperature (4.2 K) becomes very small and matches with the size of weak point pins. As a result, the highest in-field J_c at 4.2 K, 13 T ($B \perp$ tape) is observed for Ba-2.15 (figure 3-39). Figure 3-40(c) and (f) show the plan- and cross-sectional views of 15 mol% Zr-doped (Gd, Y)BCO films with Ba-2.35 with a compositional ratio (Ba-Zr/Cu ~ 0.74). As shown in figure 3-40 (c), no significant differences in nanocolumn density can be seen in comparison to Ba-2.15. However, major differences between Ba-2.15 and 2.35 can be seen in the cross-section. Ba-2.35 does not show any bottle-shaped behavior for BZO nanocolumns in the cross-section as observed in figure 3-40 (f). BZO nanocolumns appeared continuous and straight for Ba-2.35 as shown in figure 3-40(f), growing along the c -axis of (Gd, Y)BCO, with no traces of any RE_2O_3 precipitates. The BZO nanocolumn average diameter for Ba-2.35 is ~ 6.3 nm, and nanocolumn spacing is ~ 16.3 nm, leading to a matching field of ~ 7.8 T (Table 3-13). Consistent BZO nanocolumn spacing for Ba-2.15 and -2.35 validates the consistency in the c -axis lattice constant depicted in figure 3-38. This means that after Ba-2.15, the density of the nanocolumns did not increase, but in-plane texture degradation led to a lower self-field J_c which affected the in-field performance at Ba values higher than 2.15. The reason for this sharp in-plane texture degradation for Ba above 2.15 is still under study.

It can also be seen that even when the BZO nanocolumn size did not change and dopant concentration in the film did not increase, the density of nanocolumns increases for Ba-2.0 up to -2.15. However, formation of the bottle-shaped BZO nanocolumns at Ba-2.15, which is not observed with Ba-2.0, may give some indication of the reason for this finding. Preliminary results for the bottle shape in BZO nanocolumns indicate traces of rare-earth, which is indicative of some kind of substitution of rare-earth into the BZO, which could increase the volume percentage of BZO. Any claims at this point would not be appropriate and this question is a topic of an on-going study and beyond the scope of this thesis.

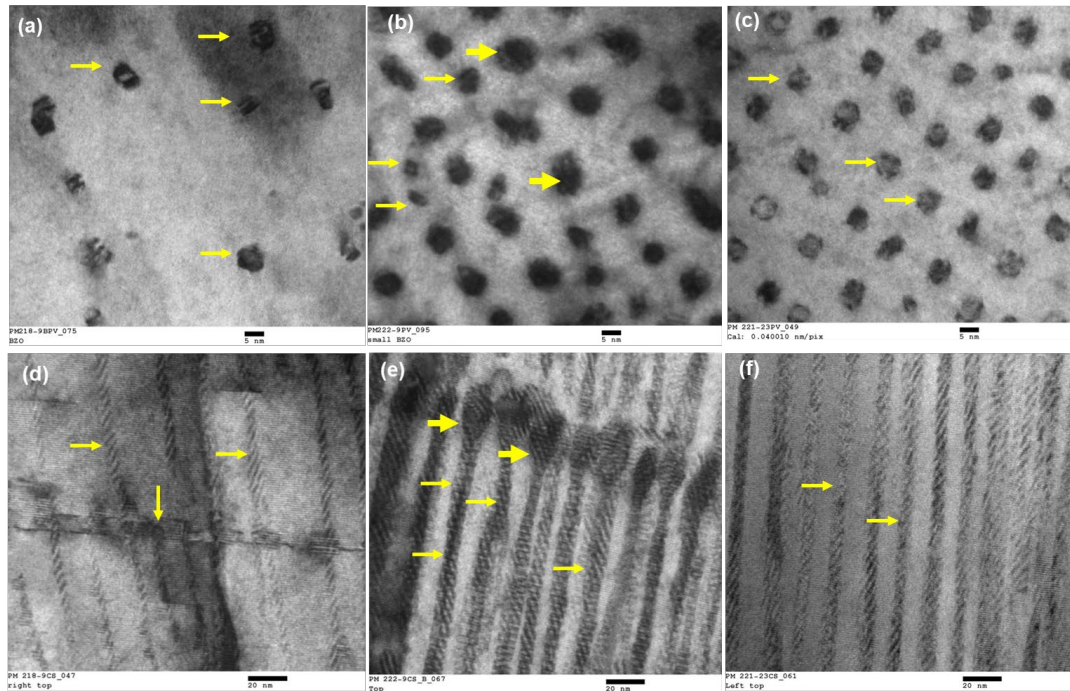


Figure 3-40. (a),(b), and (c) show TEM plan-view microstructures of 15 mol% Zr-doped (Gd, Y)BCO with Ba-2.0, Ba-2.15 and Ba-2.35 respectively. (d), (e), and (f) show their TEM cross-sectional microstructures.

Table 3-13. BaZrO₃ nanocolumn spacing and matching field of 15 mol% Zr-doped (Gd, Y)BCO with Ba-2.0 (Ba-Zr/Cu~0.62), Ba-2.15 (Ba-Zr/Cu~0.70), and Ba-2.35 (Ba-Zr/Cu~0.74).

Barium in precursor compositional ratio	Average (Ba-Zr)/Cu in film	BaZrO ₃ nanocolumn spacing (nm)	Matching field (T)
2	0.62	29.2	2.4
2.15	0.7	17	7.2
2.35	0.74	16.3	7.8

3.3.3. Effects of different levels of barium concentration on microstructural and electromagnetic properties of 4.7 μm thick, 15 mol% Hf-doped (Gd, Y)BCO films

In this section, the effects of Ba on microstructural and electromagnetic properties of 15 mol% Hf-doped (Gd, Y)BCO with film thickness of $\sim 4.7 \mu\text{m}$ are reported. The compositional ratios of all other elements (Y, Gd, Cu, Zr) in the precursor are kept constant and only Ba compositional ratios have been varied from Ba-1.97 to 2.02, 2.07, and finally up to 2.12.

3.3.3.1. Effects of Ba in precursor compositional ratio on (Ba-Hf)/Cu in films

Figure 3-41 show the (Ba-Hf)/Cu of multiple 15 mol% Hf-doped (Gd, Y)BCO films with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in precursor. Ba-, Hf-, and Cu-normalized concentrations (at%) are obtained via ICP analysis of each film. With an increase in Ba from Ba-1.97 to Ba-2.02 in the compositional ratio, a higher increase in (Ba-Hf)/Cu can be seen in the film. However, from Ba-2.02, the increase of (Ba-Hf)/Cu in the film slows down with same Ba increment in the precursor. This indicates that changing Ba in the precursor after a certain limit can influence the conversion barium from precursor to film ratio.

Increasing (Ba-Hf)/Cu should depict the increase in Ba in the film since dopant concentration is kept constant and Hf does not tend to form any other phase except BHO, in the same manner as Zr, so it should be assumed that an increase in (Ba-Hf) with increasing Ba in the precursor should cause an increase in Ba in the film.

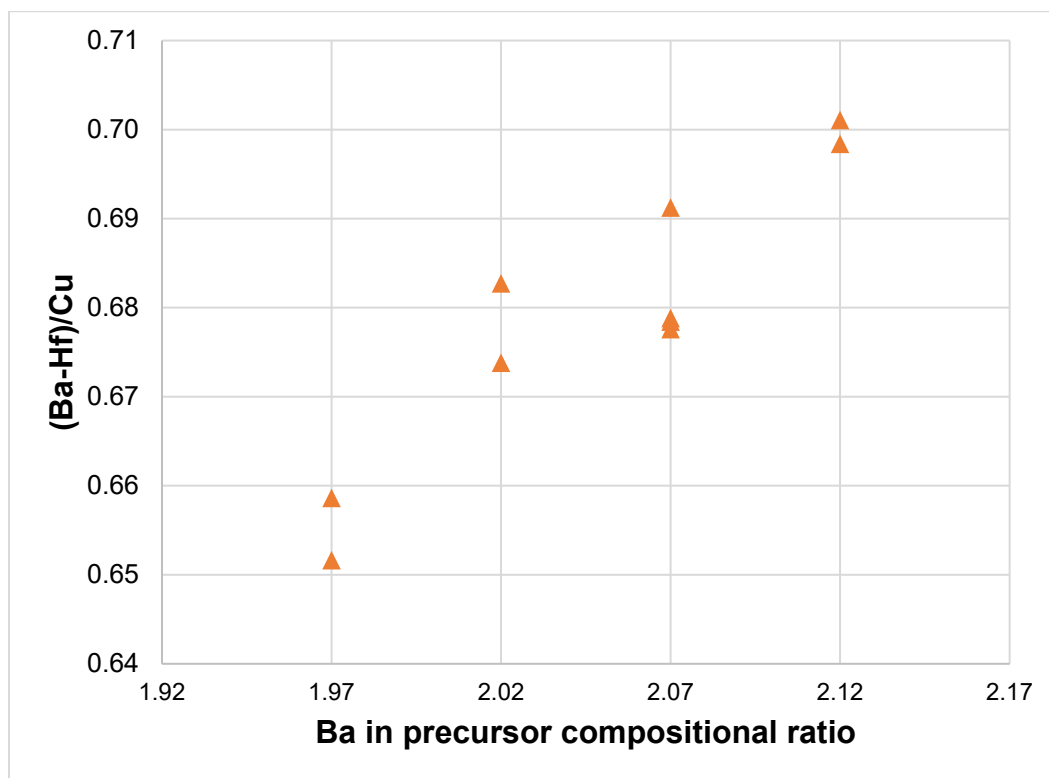


Figure 3-41. (Ba-Hf)/Cu of multiple 15 mol% hafnium (Hf)-doped (Gd, Y)BCO films with different Ba compositional ratios (1.97, 2.02, 2.07, and 2.12) in the precursor. All films used 0.025 M precursor.

In order to simplify the comparison of different microstructural and electromagnetic properties for different Ba films, the averages of (Ba-Hf)/Cu of multiple films with each Ba concentration are calculated and tabulated in table 3-14. It should be noted here that in Zr-doped study (section 3.3.2), Ba compositional ratios in the precursor were changed extensively from Ba-2.0 up to 2.35 that varied (Ba-Zr)/Cu in the film from

0.62 to 0.74, while in Hf, the Ba compositional ratios in the precursor is varied only from Ba-1.97 to 2.12; hence, the variation in (Ba-Hf)/Cu is lower, ranging from 0.66 to 0.70. It should also be noted here that in Zr doping with Ba-2.0 in the precursor compositional ratio, (Ba-Zr)/Cu was ~ 0.62 , while in Hf doping, with the even lower Ba-1.97 in the precursor compositional ratio, (Ba-Hf)/Cu is higher with an absolute value of ~ 0.66 . The reason for this difference is not very clear at this moment. It could be due to effects of different dopants on thermal stability of different elements used in the precursor or different Ba precursor batches used.

Table 3-14. Average (Ba-Hf)/Cu of multiple 15 mol% Hf-doped (Gd, Y)BCO films with the different Ba compositional ratios (1.97, 2.02, 2.07, and 2.12) in the precursor. All films used 0.025 M precursor.

	Average (Ba-Hf)/Cu
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{1.97}\text{Cu}_{2.60}\text{Hf}_{0.15}$	0.66
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.02}\text{Cu}_{2.60}\text{Hf}_{0.15}$	0.68
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.07}\text{Cu}_{2.60}\text{Hf}_{0.15}$	0.69
$\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{2.12}\text{Cu}_{2.60}\text{Hf}_{0.15}$	0.70

3.3.3.2. Effects of different levels of Ba concentration on the self-field J_c of 15 mol% Hf-doped (Gd, Y)BCO at 77 K

Figure 3-42 exhibits the transport self-field J_c at 77 K of 15 mol% Hf-doped (Gd, Y)BCO film with different Ba compositional ratios (Ba-1.97, 2.02, 2.07, and 2.12) in the precursor. The transport self-field J_c decreases with increasing amounts of Ba in the precursor compositional ratios; however, at low Ba concentration, the self-field J_c did not decrease, indicating absence of any secondary phases or *a*-axis-oriented grains, which was an issue with low amounts of Ba in Zr-doped films as shown in figures 3-35 and 3-36. The transport self-field J_c at 77 K is highest for 15 mol% Hf-doped (Gd, Y)BCO with Ba of

1.97 in the compositional ratio, giving an absolute value of $\sim 1.25 \text{ MA/cm}^2$, which is $\sim 30\%$ higher than the best self-field J_c attained with 15 mol% Zr-doped (Gd, Y)BCO with Ba-2.10 (shown in figure 3-35). As the Ba is increased from 1.97 to 2.02, 2.07, and 2.12, the 77 K self-field J_c drops to ~ 1.2 , ~ 0.9 , and 0.75 MA/cm^2 , respectively. When compared with Zr with same (Ba-M(Zr or Hf))/Cu, Hf-doped films exhibit a higher self-field J_c . For example, with (Ba-M)/Cu ~ 0.70 , the Hf-doped film shows a self-field J_c of $\sim 0.75 \text{ MA/cm}^2$, which is 17% higher than that of the Zr-doped film ($J_c \sim 0.64 \text{ MA/cm}^2$).

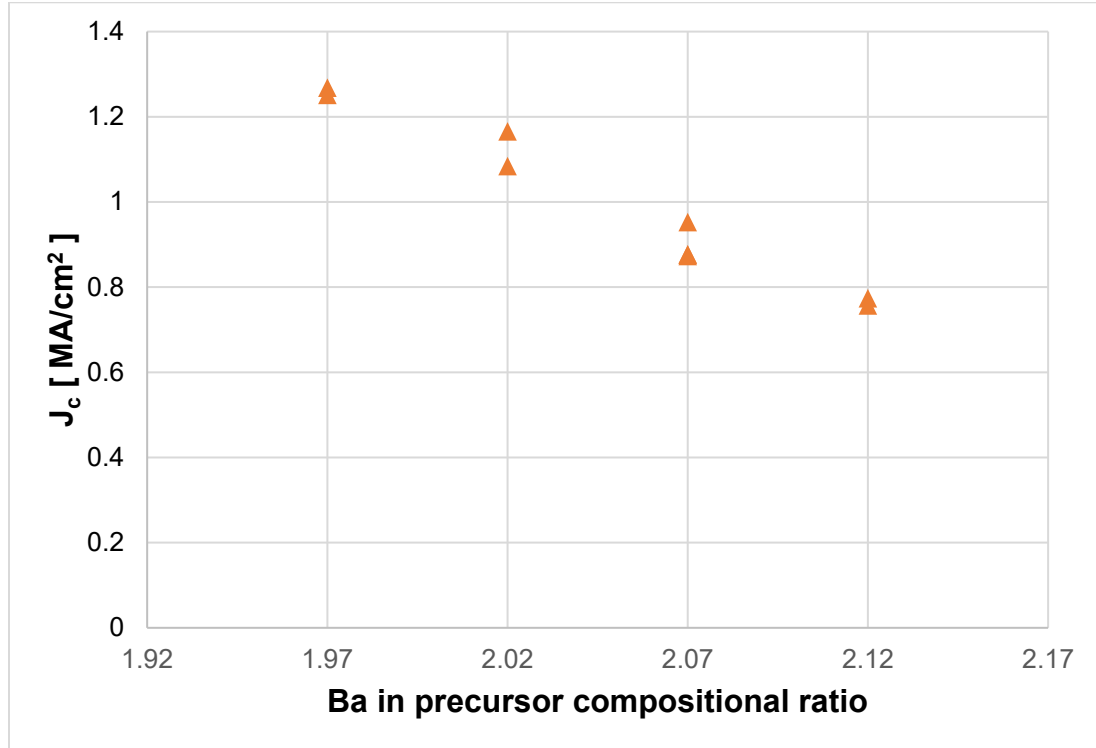


Figure 3-42. Transport J_c at 77 K and 0 T of 15 mol% Hf-doped (Gd, Y)BCO with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in precursor. All films are $\sim 4.7 \mu\text{m}$ thick and used 0.025 M precursor.

In order to check the formation of a -axis grains with changes in Ba, θ - 2θ diffraction patterns of 15 mol% Hf-doped (Gd, Y)BCO films with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in the precursor were conducted in the range of 45° to 48° as shown in figure 3-43. The absence of the (200) peak in figure 3-43 at all Ba concentrations confirms the absence of a -axis oriented grains. This is important in the sense that even with such low (Ba-Hf)/Cu ~ 0.66 for Ba-1.97, there is no formation of any mis-oriented grains, while in 15 mol% Zr-doped (Gd, Y)BCO with relatively higher (Ba-Zr)/Cu ~ 0.68 , a high number of a -grains was present (figure 3-36). This can be due to lower lattice mismatch of BHO with (Gd, Y)BCO when compared with the mismatch of BZO with (Gd, Y)BCO. Lower lattice mismatch appears to lead to smoother films and avoid formation of mis-oriented grains. Also lower lattice mismatch can avoid deterioration of texture.

Another important observation to note in figure 3-43 is the lack of change in 2θ value of the (006) peak of 15 mol% Hf-doped (Gd, Y)BCO films with different amounts of Ba, which indicates no change in the c -axis lattice constant. This will be discussed in detail in the next section.

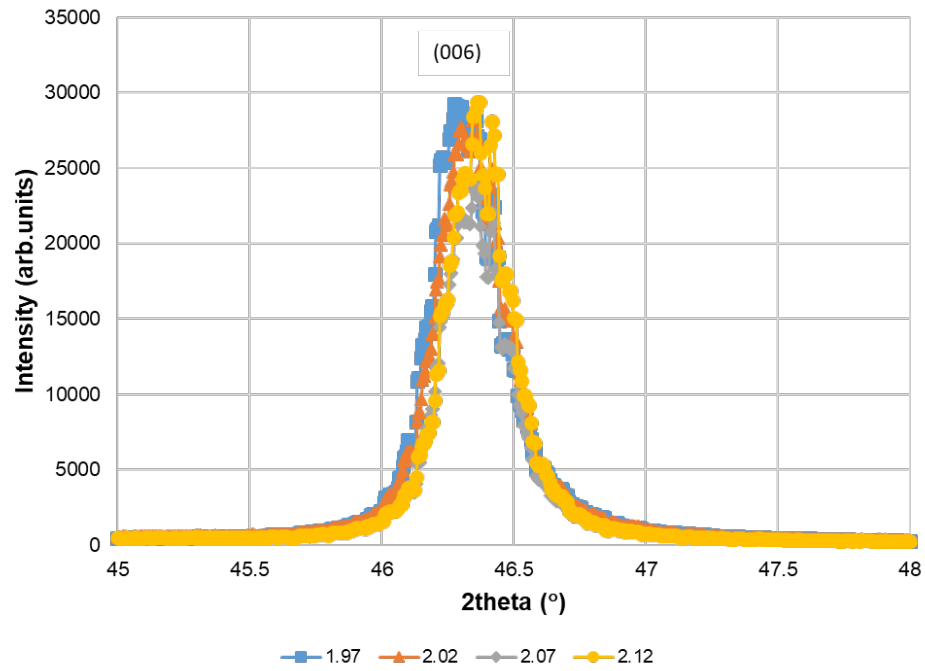


Figure 3-43. XRD theta-2theta diffraction pattern of 15 mol% Hf-doped (Gd, Y)BCO with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in precursor.

3.3.3.3. Effect of different levels of Ba concentration on texture and *c*-axis lattice constant of 15 mol% Hf-doped (Gd, Y)BCO

Figure 3-44 shows the in-plane and out-of-plane texture values of the 15 mol% Hf-doped (Gd, Y)BCO films with Ba-1.97, 2.02, 2.07, and 2.12 compositional ratios in the precursor. Both in-plane and out-of-plane texture values appear very consistent and independent of Ba in the precursor. In-plane texture values for Ba-1.97 to 2.12 are in the range of $\sim 4^\circ$ to 5° , which is similar to the texture of Ba-2.15 15 mol% Zr-doped (Gd, Y)BCO films; which performed best at 4.2 K and 13 T. A deterioration of the in-plane texture was seen in 15 mol% Zr-doped (Gd, Y)BCO films with (Ba-Zr)/Cu above 0.70. Since 15 mol% Hf-doped (Gd, Y)BCO films with (Ba-Hf)/Cu higher than 0.70 were not

prepared in this work, it is difficult to say if in-plane texture would be constant with further increase in barium concentration.

The out-of-plane texture of 15 mol% Hf-doped (Gd, Y)BCO films is $\sim 1^\circ$, independent of Ba variations in the precursor. This absolute value is better than the out-of-plane texture of 15 mol% Zr-doped (Gd, Y)BCO with any Ba content. It certainly appears that the crystallinity is slightly better in Hf-doped (Gd, Y)BCO films, which could be attributed to a lower mismatch between BHO and (Gd, Y)BCO that avoids deterioration of crystallinity in the film.

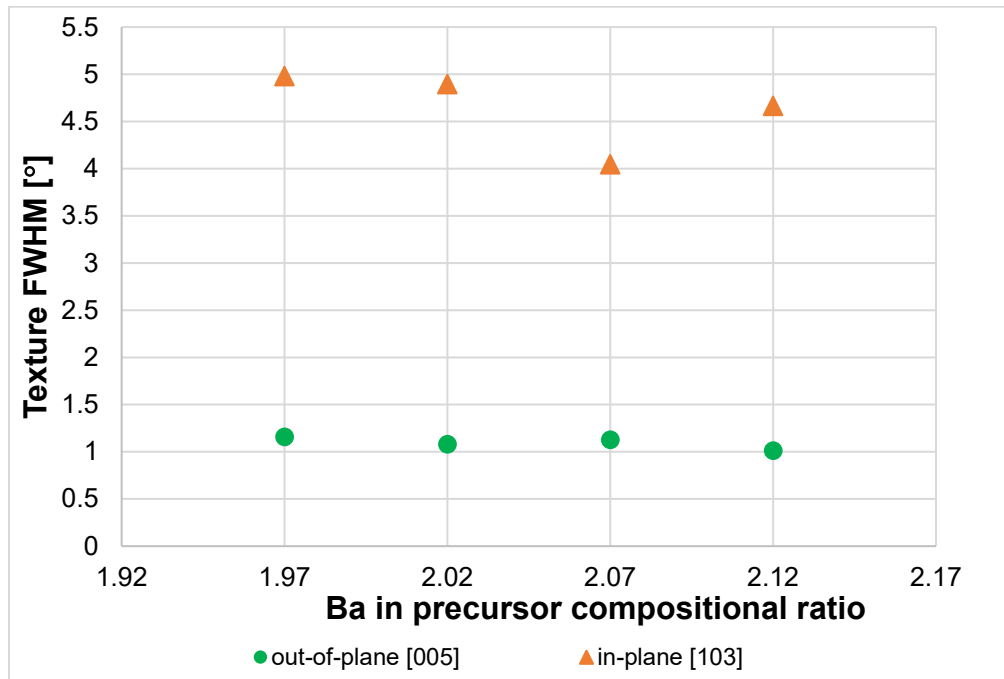


Figure 3-44. Out-of-plane and in-plane texture (shown in FWHM) of the 15 mol% Hf-doped (Gd, Y)BCO with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in precursor.

Such consistent texture values do not explain why the 77 K self field J_c decreased with increasing Ba concentrations in the Hf-doped films. In order to further investigate this

finding, the c -axis lattice constants of 15 mol% Hf-doped (Gd, Y)BCO with different amounts of Ba (1.97, 2.02, 2.07, and 2.12) in the compositional ratios were calculated from the (00 l) peaks of (Gd, Y)BCO using a least-squares fit to the Nelson-Riley function [105] and are depicted in figure 3-45. As shown in figure 3-45, the c -axis lattice constant of the 15 mol% Hf-doped films seems to be almost constant with increasing amounts of Ba in the film. This is in contrast to that observed in 15 mol% Zr-doped (Gd, Y)BCO films in which when (Ba-Zr)/Cu was maintained between 0.66 and 0.70, a sharp and rapid increase in c -axis lattice constant was observed (figure 3-38). The c -axis lattice constant of different Ba normalized concentrations from 1.97 to 2.12 in 15 mol% Hf-doped (Gd, Y)BCO film is in the narrow range of 11.35 Å to 11.748 Å. The absolute value of the c -axis lattice constant for 15 mol% Hf-doped (Gd, Y)BCO film is similar to that of the 15 mol% Zr-doped (Gd, Y)BCO with Ba-2.15.

Consistent values of the c -axis lattice constant validates consistency in the in-plane and out-of-plane texture but does not explain the drop in 77 K self-field J_c with increasing Ba in the 15 mol% Hf-doped (Gd, Y)BCO film.

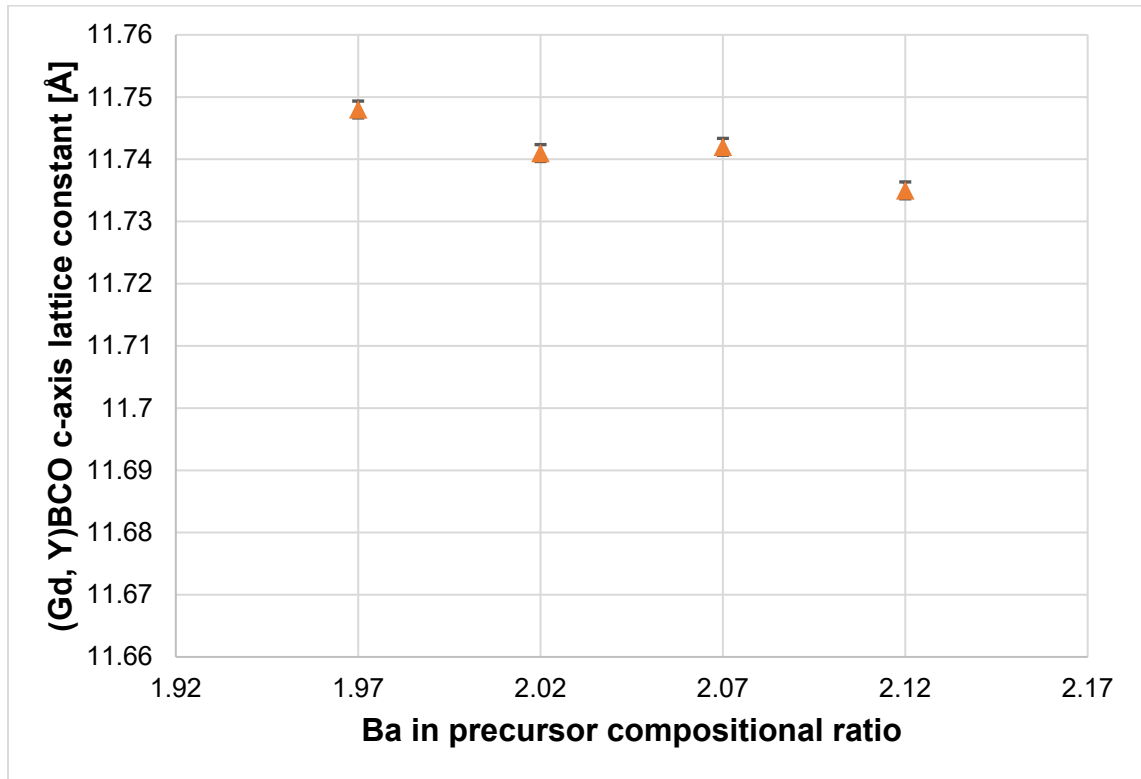


Figure 3-45. The c -lattice parameter of 15 mol% Hf-doped (Gd, Y)BCO with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in precursor.

3.3.3.4. Effects of different levels of Ba concentration on the in-field J_c of 15 mol% Zr-doped (Gd, Y)BCO at 4.2 K

Figure 3-46 illustrates the magnetic J_c of the 15 mol% Hf-doped (Gd, Y)BCO with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in the precursor. All 15 mol% Hf-doped (Gd, Y)BCO films show a consistent J_c at 4.2 K and 13 T ($B \perp$ tape) in the range of 4 to 4.87 MA/cm², independent of the amount of Ba used in the precursor. This consistency in the in-field J_c at 4.2 K, when seen in conjunction with the decrease in 77 K self-field J_c , indicates an increase in pinning centers with an increase in Ba. Otherwise, in-field J_c should have followed the trend of the 77 K self-field J_c as shown in figure 3-42.

However, it is important to note that even though the pinning centers increased with the increase in Ba, there is no evidence of any change in texture quality or *c*-axis lattice constant. Also the absolute values of the highest in-field J_c ($\sim 4.84 \text{ MA/cm}^2$) for the 15 mol% Hf-doped (Gd, Y)BCO film (Ba-2.12)(Ba-Hf/Cu -0.70) at 4.2 K and 13 T ($B \perp \text{tape}$) is 32 % lower than the best in-field J_c ($\sim 7.14 \text{ MA/cm}^2$) of the 15 mol% Zr-doped (Gd, Y)BCO film (Ba-2.15) (Ba-Zr/Cu – 0.70). Although the self-field J_c of 15 mol% Hf-doped films was 17% higher for the same (Ba-M)/Cu-0.70, the effectiveness of pinning in the 15 mol% Zr-doped film at 13 T overshadowed the self-field J_c effect and led to a 32 % higher in-field J_c .

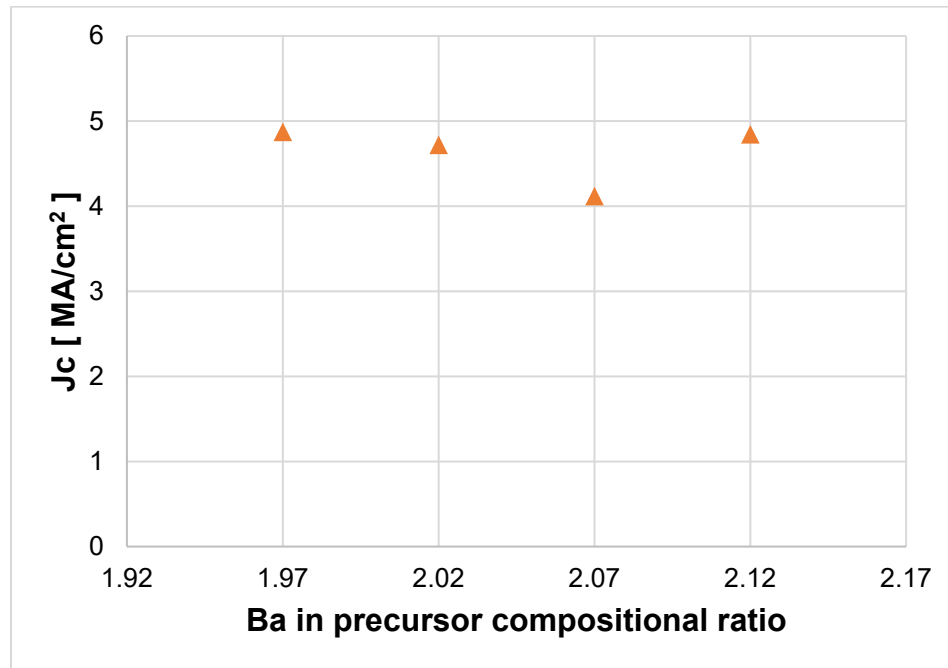


Figure 3-46. Magnetic J_c at 4.2 K and 13 T ($B \perp \text{tape}$) for 15 mol% Hf-doped (Gd, Y)BCO with different Ba compositional ratios of 1.97, 2.02, 2.07, and 2.12 in precursor.

3.3.4. Record-high transport critical current achieved in 15 mol% Zr-doped 4+ μm thick (Gd, Y)BCO in low temperature regime (50 -4.2 K)

3.3.4.1 Record-high transport critical current achieved in 15 mol% Zr-doped 4+ μm thick (Gd, Y)BCO at 30 - 50 K

The transport I_c angular dependence of 15 mol% Zr-doped (Gd, Y)BCO film at 30 K, 40 K and 50 K in 3 T magnetic field is shown in figure 3-47 [134]. A record-high critical current value of 8705 A/12 mm has been achieved at 30 K, 3 T ($B \parallel c$ -axis) which is more than two times higher than the best value of 3963 A/12 mm obtained in 2.2 μm thick, 20 mol% Zr added GdYBCO film processed in two passes using conventional MOCVD [72]. This value is also 2.7 times higher than the previously achieved critical current value obtained using A-MOCVD in a 2 μm thick, 20 mol% Zr added GdYBCO film processed in a single pass. Also, it is more than 7 times higher than the critical current value of 1072 A/12 mm obtained in 0.9 μm thick, 15 mol% Zr added GdYBCO film made by conventional MOCVD [116]. The critical current density at 30 K, 3T is 15.11 MA/cm², which is about the same as the highest value of 15 MA/cm² attained in 2.2 μm thick, 20 mol% Zr added GdYBCO film processed in two passes [72]. This J_c value also compares very well with the record high J_c value of 20.1 MA/cm² reported at 30 K, 3T in 0.9 μm thick, 25 mol% Zr added GdYBCO film made by conventional MOCVD [135].

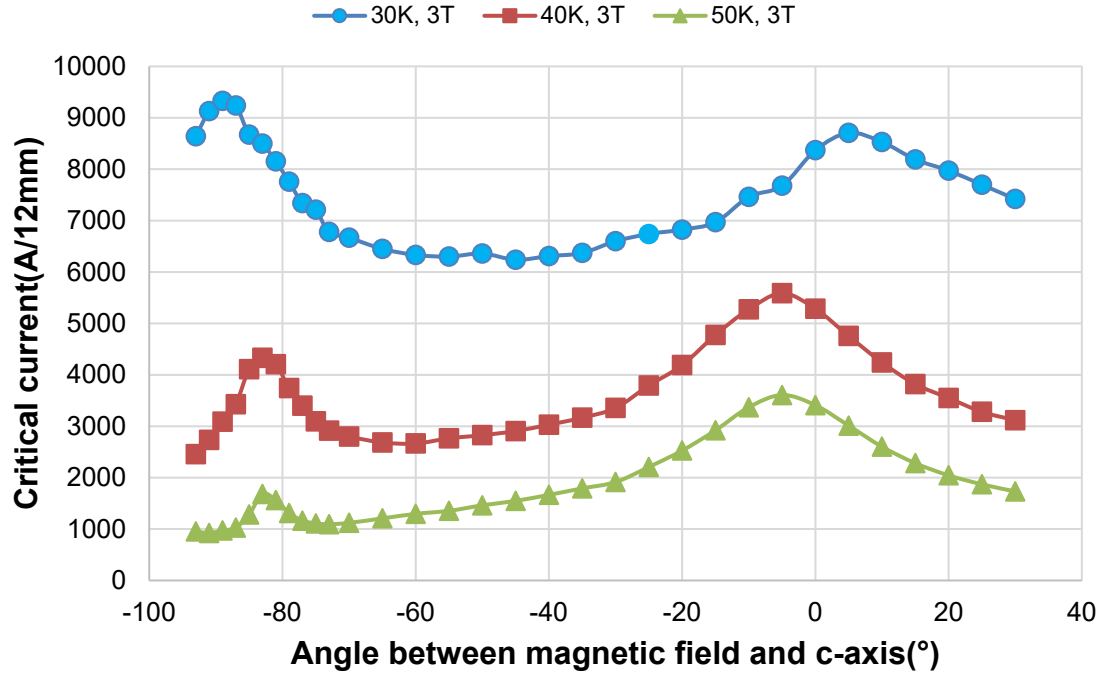


Figure 3-47. Angular dependence of transport critical current of a 5 μm GdYBCO tape with 15 mol% Zr addition at 30 K, 40 K and 50 K in 3 T magnetic field.

Shown in figure 3-48 is the critical current in magnetic fields up to 9T applied along the c-axis at 30, 40 and 50 K [134]. At 3 T, record high critical current values of 5586 A/12 mm and 3606 A/12 mm have been measured at 40 K and 50 K, respectively, which is 1.9 times higher than the best reported value in 2.2 μm thick, 20 mol% Zr added GdYBCO film processed in two passes using conventional MOCVD [72]. The corresponding J_c values are 9.69 MA/cm² and 6.26 MA/cm² at 40 K and 50 K respectively. The engineering current density (J_e) values (considering a typical 40 μm thick copper stabilizer) at 30 K, 40 K and 50 K in magnetic field 3T ($B \parallel c$) are 7068 A/mm², 4535 A/mm² and 2928 A/mm² respectively. The engineering current density at 40 K, 3 T is a factor of 1.9 times higher than the best value of 2360 A/mm² reported in the 2.2 μm thick, 20 mol% Zr added GdYBCO film and more than 7 times higher than that of the best commercial HTS tapes

reported in a recent study [72]. Such high J_c values offer an opportunity for a significant reduction in the amount of superconductor tape needed for superconducting devices which in turn reduces the cost for commercial applications.

The minimum value of critical current ($I_{c,min}$) in angular dependence measurements is an important parameter since a wide range of field orientations can be present in superconducting coils near the end turns. The $I_{c,min}$ value at 30 K, 3 T is 6238 A/12 mm, which is 1.9 times higher than $I_{c,min}$ value of 2.2 μm thick 20 mol% Zr added GdYBCO film grown by conventional MOCVD [72]. Therefore, the entire angular I_c dependence shown in Figure 3-47 is about a factor of two higher than that reported in [72].

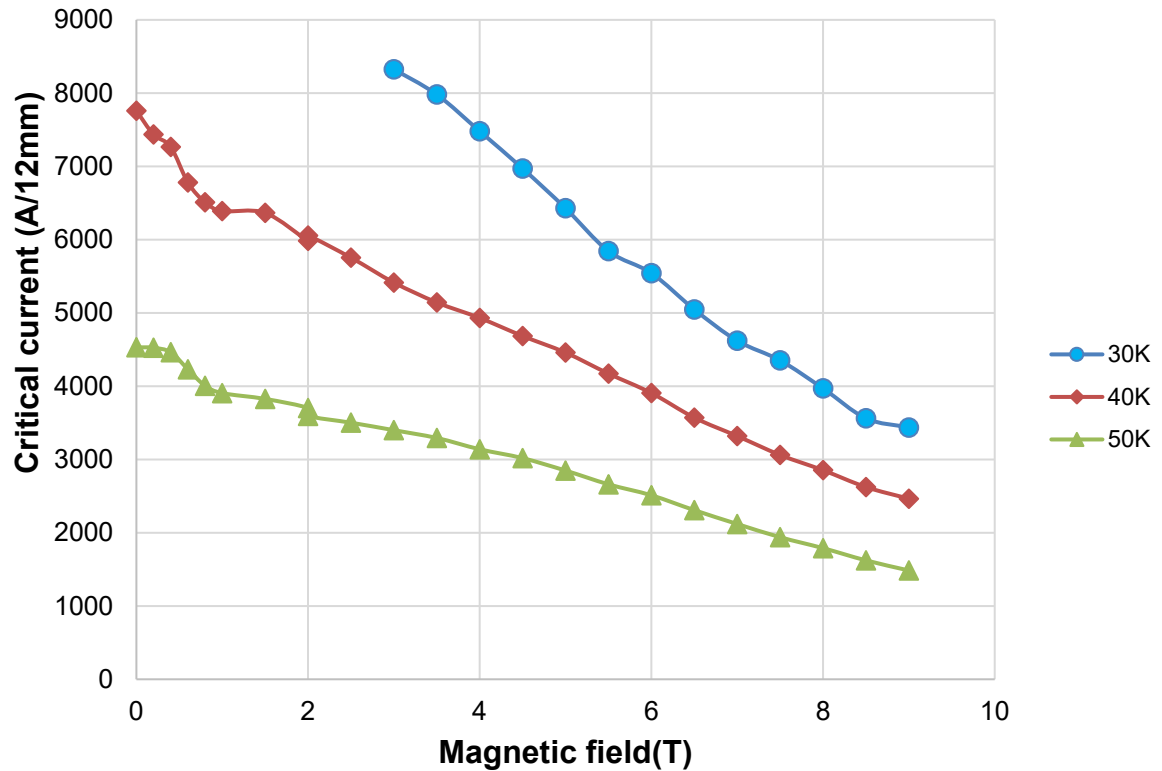


Figure 3-48. Transport critical current of a 5 μm GdYBCO tape with 15 mol% Zr addition in magnetic field up to 9 T applied along the c -axis at 30 K, 40 K and 50 K.

3.3.4.2. Record-high transport critical current properties achieved in 15 mol% Zr-doped 4+ μm thick (Gd, Y)BCO at 4.2 K

Two different samples were measured independently at Lawrence Berkeley National Laboratory (LBNL) and the National High Magnetic Field Laboratory (NHMFL) at 4.2 K, in magnetic fields up to 15 T applied along the c -axis. Both samples were of the same nominal composition and 15% Zr addition and were deposited separately in A-MOCVD as two independent samples, resulting thicknesses of 4.6 and 4.3 μm , respectively. The results are summarized in figure 3-49 as a function of applied magnetic field parallel to c -axis ($B \parallel c$ -axis) [136]. Remarkably, high critical current values of 2247 and 2119 A/4 mm width have been measured at 4.2 K, 14 T for the two samples. These values are higher by a factor of >2 than the best-reported value in 3.2 μm thick, 20 mol% Zr-doped GdYBCO film processed in three passes using conventional MOCVD and more than five times higher than the commercial HTS tapes reported in a recent study [131,137]. The corresponding J_c values are 12.21 MA/cm² and 12.32 MA/cm² respectively. The pinning force (F_p) at 4.2 K, 14 T is 1.7 TN/m³. This value is the same as the highest value reported in a 0.9 μm thick, 15 mol% Zr added GdYBCO film processed in single pass using conventional MOCVD [138]. This is significant in the sense that the same pinning force is achieved in samples with more than a four-fold increase in thickness.

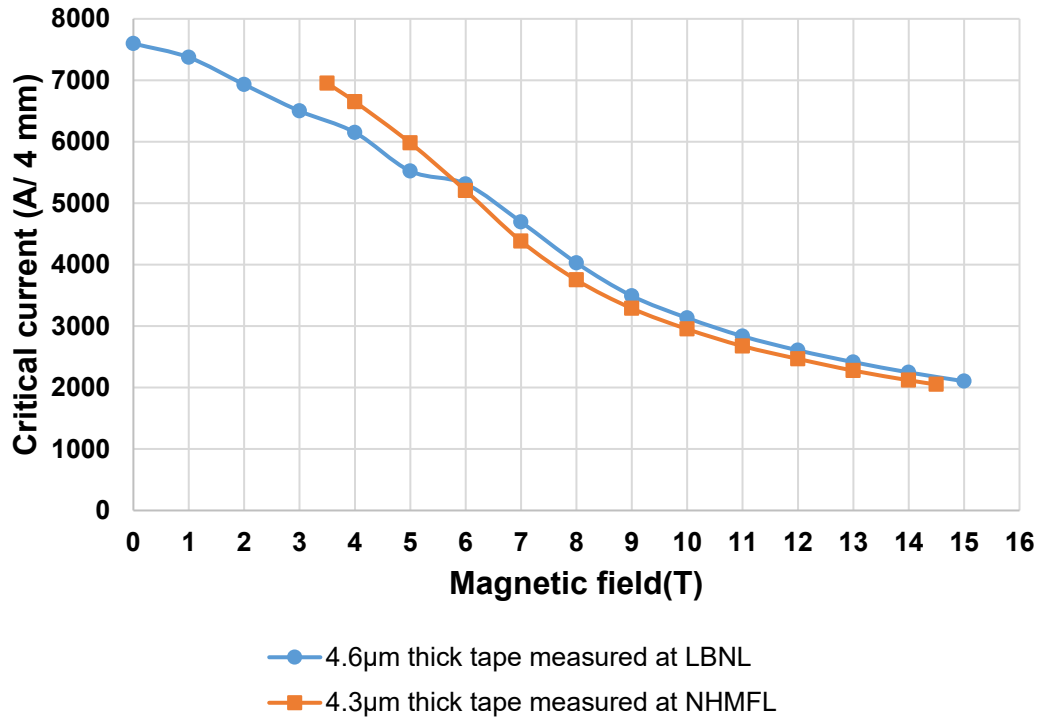


Figure 3-49. Transport critical current versus magnetic field applied along *c*-axis at 4.2 K. The very high J_c values achieved directly impact the engineering current density.

(J_c)—one of the major metrics for most 4.2 K applications. The measured samples were deposited on substrates with Hastelloy and buffer stack thicknesses of 50 μm and 0.2 μm , respectively, $\sim 3 \mu\text{m}$ cap silver layer and $\sim 40 \mu\text{m}$ of surround copper stabilizer. Utilizing these values, the corresponding engineering current density values for the two samples at 4.2 K, 14 T ($B \parallel c$ -axis) are 5.48 kA/mm^2 and 5.13 kA/mm^2 , respectively, which again constitutes more than a two-fold increase compared to the best value of 2.5 kA/mm^2 reported in the 3.2 μm thick, 20 mol% Zr added GdYBCO film [131]. The J_c versus field values of these two samples are plotted in figure 3-50 against other commercial superconductor technologies available for 4.2 K operation, i.e., on a plot of J_c versus B of various 4.2 K superconductors, as made and maintained by Lee [136]. At 15 T, the J_c of

the thick film REBCO is over five times higher than the best reported J_e value of Nb_3Sn which is the primary superconductor used now in high-field applications. These results clearly demonstrate the potential of REBCO coated conductors for use in 4.2 K in-field applications.

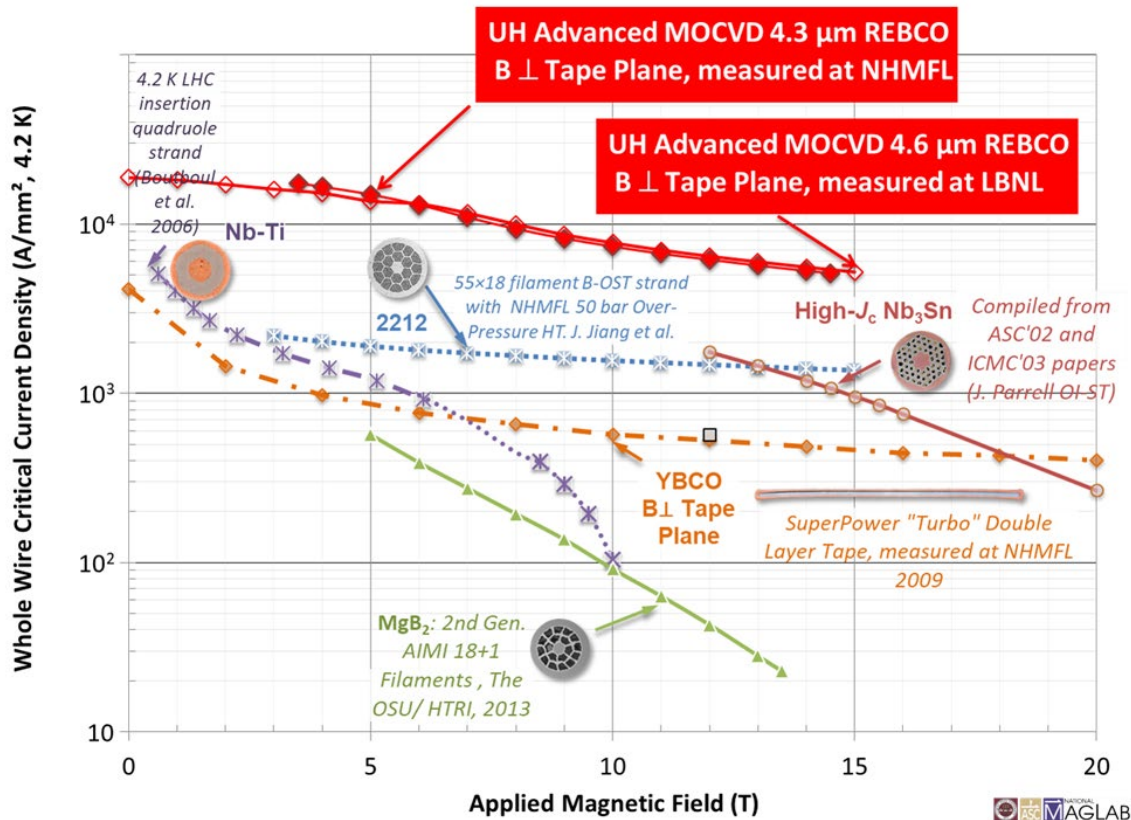


Figure 3-50. Engineering current density (J_e) of UH REBCO samples versus magnetic fields applied along the c -axis at 4.2 K, compared to other superconductor technologies.

3.3.5. Summary

This section focused on the achievement of high critical currents performance in thick (3.8 μm and above) (Gd, Y)BCO films. Firstly, the effect of different dopant

concentrations on the in-field performance at low temperatures (30 and 4.2 K) were investigated. It was found that at high fields (above 2.5 T), 15 mol% doped (Gd, Y)BCO shows much better performance than undoped (Gd, Y)BCO and 5 mol% doped (Gd, Y)BCO. Two studies were constructed on studying the effect of different barium concentration with two different dopants (zirconium and hafnium) at constant high dopant concentration (15 mol%). Further, some selected high performance 15 mol% Zr-doped 4+ μm thick (Gd, Y)BCO films were measured for transport critical current at 4.2 K (up to 15 T) and 30 K (up to 9 T).

Considering the results of these studies, the following conclusions can be drawn:

- (1) At lower temperature (30 K and 4.2 K), in all applied magnetic fields perpendicular to tape, undoped (Gd, Y)BCO shows very low critical current density due to a lower density of pinning centers. 5 mol% Zr-doped (Gd, Y)BCO shows high performance till low fields (~ 2 T), after which 15 mol% Zr-doped (Gd, Y)BCO dominates. 15 mol% Zr-doped film shows ~ 1.7 times and ~ 5 times higher J_c than 5 mol% Zr-doped and undoped (Gd, Y)BCO films respectively at both 30 and 4.2 K in a magnetic field of 13 T ($B \perp$ tape). Also, 15 mol% Zr-doped film shows a higher retention factor at both temperatures in all magnetic fields. This happens as higher dopant concentration with optimum barium leads to high density of nanocolumns which generates more weak pinning defects which act as effective pinning centers at low temperatures and high fields.
- (2) Varying barium in compositional ratio in 15 mol% Zr-doped (Gd, Y)BCO does affect its microstructure and electromagnetic properties. When barium increases from 2.0 till 2.10, self-field J_c increases due to decrease in secondary phases and a -

axis oriented grains. While with further increase in barium, self-field J_c decreases due to increase in c -axis lattice constant (only for Ba-2.15) and deterioration of in-plane texture (above Ba-2.15). 77 K self-field J_c is the highest with Ba-2.10 while at 4.2 K, 13 T ($B \perp$ tape), Ba-2.15 in 15 mol% Zr-doped film shows highest J_c of $\sim 7 \text{ MA/cm}^2$. This is due to formation of continuous nanocolumns and increase in its density with increase in barium.

- (3) TEM analysis of films with different Ba (2.0, 2.15 and 2.35) shows interesting results. With Ba-2.0, nanocolumns are not continuous and are broken by RE_2O_3 precipitates and secondary phases while with increasing barium to 2.15, nanocolumns becomes continuous (with both bottle shape and normal diameter along length of nanocolumns); also, their density increases while no trace of RE_2O_3 precipitates is observed. This formation of continuous nanocolumns with higher density without significantly deteriorating the self-field J_c led to an increase in in-field performance as mentioned in (2). With further increasing barium to Ba-2.35, nanocolumns remains continuous but bottle shape disappears and nanocolumnar density and size remain similar and still no RE_2O_3 precipitates are observed. Different microstructural changes are seen at different Ba content: increase in nanocolumnar density when Ba increases from 2.0 to 2.15 (even though dopant concentration (15%) is same in both) while constant nanocolumnar density and sizes when barium increases from 2.15 to 2.35. Also, the reason behind increase in in-plane texture degradation even when c -axis lattice constant is similar when barium increases from 2.15 till 2.35 is not clear. This research is a part of on-going study.

- (4) 15 mol% Hf-doped (Gd, Y)BCO behaves different than 15 % Zr-doped (Gd, Y)BCO in terms of effect of barium. In Hf-doped films, increase barium compositional ratios (1.97 to 2.12) does not affect in-plane texture, out-of-plane texture and *c*-axis lattice constant. Out-of-plane texture of 15 mol% Hf-doped (Gd, Y)BCO is independent of Ba content and shows an absolute value of $\sim 1^\circ$ which is better than out-of-plane texture of 15 mol% Zr-doped (Gd, Y)BCO. Also, with lower (Ba-Hf)/Cu, Hf-doped films do not form any mis-oriented grains.
- (5) Hf-doped films shows a decrease in 77 K self-field J_c with increasing barium but no related systematic change in either texture or *c*-axis lattice constant. However, it is interesting to note that, at 4.2 K, all films with different barium in 15 mol% Hf, exhibit a similar $J_c \sim 4\text{--}4.8 \text{ MA/cm}^2$. Increase in in-field J_c of high barium samples, to a same level at 4.2 K, 13 T in spite of their lower 77 K self-field J_c points to an increase of pinning defects with higher barium levels. The reason behind decrease of self-field J_c with increase barium is still a part of on-going research study. Generally, comparing 15 mol% Hf-doped and 15 mol% Zr-doped (Gd, Y)BCO films with different barium content, Hf-doped films with same (Ba-M)/Cu ~ 0.70 perform better at 77 K self-field (17 % higher J_c than Zr-doped (Gd, Y)BCO films) while the 15 mol% Zr-doped film exhibits 32 % higher J_c at 4.2 K, 13 T ($B \perp$ tape),
- (6) A 4.8 μm thick, 15 mol% Zr-doped (Gd, Y)BCO tape showed record-high critical currents of 8705 A/12 mm, 5586 A/12 mm and 3606 A/12 mm at 30 K, 40 K and 50 K respectively in a magnetic field of 3 T ($B \parallel c$ -axis) which are approximately two times higher than the best values reported in literature. The corresponding engineering current density (J_e) values are 7068 A/mm², 4535 A/mm² and 2928

A/mm² at 30 K, 40 K and 50 K respectively. Engineering critical current density (J_e) of this tape at 40 K, 3 T is more than 7 times higher than that of the best commercial HTS tapes.

- (7) Critical currents of two different 4+ μ m thick, 15 mol% Zr-doped (Gd,Y)BaCuO tapes were measured at low temperature and high fields at LBNL and NHMFL. Remarkably, high critical currents of 2247 A/4 mm and 2119 A/4 mm have been obtained at 4.2 K, in a magnetic field of 14 T ($B \parallel c$ -axis), which are approximately a factor of two higher than the best values reported in the literature. High critical current density of over 12 MA/cm² and pinning force of 1.7 TN/m³ have been achieved. The engineering current density (J_e) value (considering a typical 40 μ m thick copper stabilizer) of over 5 kA/mm² has been achieved at 4.2 K, 14 T ($B \parallel c$ -axis) which is more than five times higher than that of Nb₃Sn and nearly four times higher than the highest reported value of all superconductors other than REBCO at this field and temperature. Such a remarkable performance reveals potential for the HTS technology to be utilized in future magnets for various applications requiring 4.2 K operating temperature and very high fields.

3.4. Improving precursor to film conversion efficiency to reduce cost of REBCO films

All applications of REBCO require low-cost, long-length 2G-HTS tapes with high critical current and consistent performance. Although there has been tremendous progress in manufacturing several kilometers of REBCO with consistent self-field critical current[93,95,137], high price/performance metric, expressed as \$/kA-m, is an impediment in its commercial viability when low-temperature superconductors and copper are available as inexpensive options.

The high cost of organometallic compounds used in the precursor is one of the major contributors in the production cost of REBCO. Conventional MOCVD suffers from low precursor-to-film conversion efficiency (10-15%), i.e., a fraction of cations deposited on film relative to the cation content in the precursor. Using a reactor design similar to A-MOCVD and using double side growth, Zhao R et al. have reported doubling the precursor utilization ratio of MOCVD to 31% [139].

Some research groups have modeled the flow dynamics of horizontal MOCVD reactors for growth of GaAs, and had shown the effect of different deposition parameters such as flow, pressure, reactor geometry on the growth rate and its uniformity along length and width of substrate [140,141]. Previously extensive flow dynamics simulations were conducted for an Advanced MOCVD reactor geometry to find the effect of different channel height with different flow on the precursor-to-film conversion efficiency of different reactants [141]. The channel height and flow values used in this model were similar to actual values that would be used in REBCO deposition in A-MOCVD system. Due to complexity of (Gd, Y)BCO growth and the lack of all properties of this system, GaAs growth was used in this model. The following results shown in figure 3-51 reveals a

substantial improvement in the efficiency of incorporation of gallium in the film when using different flows and channel heights. A main finding from the model is that with decreasing channel height, a lower precursor flow results in a better precursor-to-film efficiency. Although the organometallics used in REBCO growth have different diffusion coefficients from those used in the model for GaAs, the results showing a substantial change in concentration profile by variation of channel height and flow are very encouraging. The objective of this work is to improve the concentration profile over substrate by reducing the channel height and flow accordingly, while maintaining the deposition rate in a range that does not deteriorate REBCO growth.

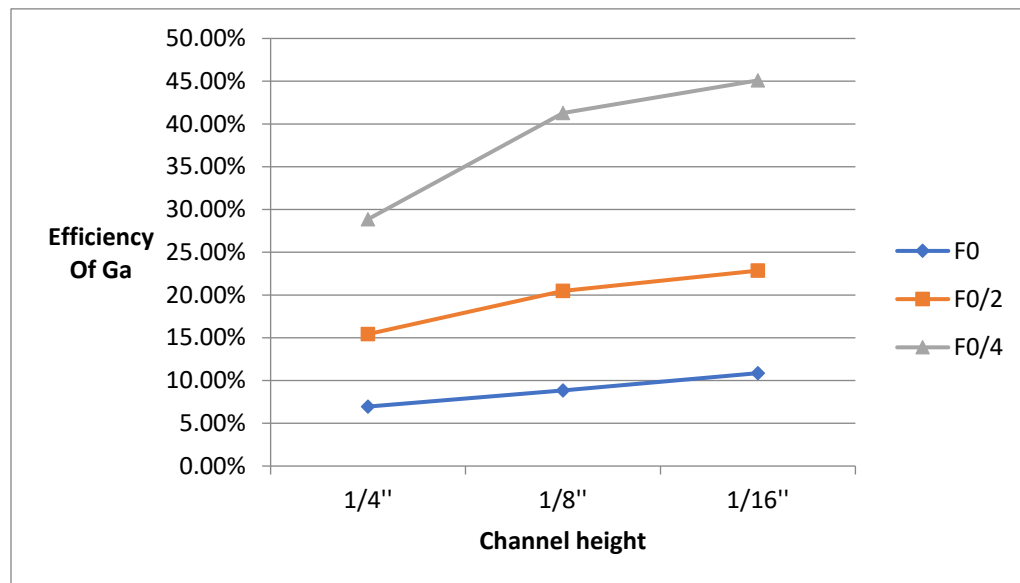


Figure 3-51. Comparison of the precursor-to-film conversion efficiency of gallium deposition with different channel height and flow (F0, F0/2 and F0/4) in A-MOCVD as predicted by model.

In this study, A-MOCVD reactor has been used to grow over 3 μm thick 5 mol% Zr doped REBCO films (0.05 M), with two different precursor flow conditions (1X and 0.5X flow) and 1/8" channel height, while all other process parameters

kept constant. The reason for choosing 0.05 M over 0.025 M is the higher deposition rate that can be achieved with 0.05 M without any degradation in its electromagnetic properties as shown in table 3-5 (result section 3.2.2.1.1.). The main objective of this study is to investigate the possibility of growing thick REBCO films with high precursor-to-film conversion efficiency, without degrading their electromagnetic and microstructural properties. If such an objective can be achieved, it will substantially reduce the production cost of 2G-HTS, making it more commercially viable.

3.4.1. Effect of flow on precursor-to-film conversion efficiency and self field J_c at 77 K

Table 3-15 provides a comparison of films grown in conventional MOCVD and A-MOCVD reactor ($\frac{1}{8}$ " channel and 1X precursor flow and $\frac{1}{8}$ " channel and 0.5X precursor flow). The films compared were grown using the same molarity of precursor (0.05 M) and same Zr content (5 mol.%). As shown in the Table 3-15, in conventional MOCVD, 0.75 μm thick doped (Gd, Y)BCO film is grown per milliliter of precursor solution per centimeter length, at a deposition rate of 100 nm/min. Consequently, the precursor-to-film conversion efficiency is $\sim 11\%$ in the conventional MOCVD reactor; such a poor efficiency leads to a high production cost because of the high cost of MOCVD precursors. In comparison, in A-MOCVD, films are grown at 1.84 and 3.03 $\mu\text{m}/\text{ml}/\text{cm}$ with 1X flow and 0.5X flow respectively with corresponding deposition rates of 240 nm/min and 190 nm/min. The corresponding precursor-to-film conversion efficiency values are $\sim 27\%$ at 1X precursor flow and $\sim 45\%$ using 0.5X flow in the A-MOCVD reactor. These values are 2X and 4X higher than the precursor-to-film conversion efficiency in conventional MOCVD.

While the deposition rate decreases by 21% when the precursor flow is reduced to half, the precursor-to-film conversion efficiency is improved by 67%. This result is consistent with the increase in precursor-to-film conversion efficiency with lower flows predicted by the model described in figure 3-51. This is a remarkable result since 4+ μm thick doped (Gd,Y)BaCuO films have been demonstrated with double deposition rate and 4X improvement in precursor conversion efficiency. This achievement can lead to substantial reduction in the cost of REBCO tapes made by MOCVD.

While increasing precursor-to-film conversion efficiency to 45%, a good J_c of 1.89 MA/cm² is achieved with 0.5X precursor flow by A-MOCVD which is better than even the performance of films with 1X flow (1.69 MA/cm²). However, the J_c of this 4+ μm thick film made by A-MOCVD is lower than that of the 0.9 μm thick film deposited by conventional MOCVD. Since J_c values as high as 3 MA/cm² have been achieved in 4+ μm thick undoped films made by A-MOCVD as shown in Figure 3-2 (section 3.1.1.), we expect similar high values can be achieved while maintaining the 45% precursor-to-film conversion efficiency.

Table 3-15. Comparison of precursor conversion efficiency, critical current and deposition details of this work done using A-MOCVD and previous results obtained using conventional MOCVD.

Reference	[116,142]	This work	This work
Reactor	MOCVD	A-MOCVD 1/8" channel and 1X flow	A-MOCVD 1/8" channel and 0.5X flow
Molarity of precursor	0.05 M	0.05 M	0.05 M
Zr molar content	5%	5%	5%
Film thickness [μm]	0.9	3	4.9
Thickness per unit length to precursor flow [$\mu\text{m}/\text{ml}/\text{cm}$]	0.75	1.84	3.03
I_c at 77 K, 0 T [A/12mm]	430	610	1104
J_c at 77 K, 0 T [MA/cm^2]	3.6	1.69	1.89
Precursor to film conversion efficiency	11%	27%	45%
Deposition rate [nm/min]	100	240	194

3.4.2. Effect of flow on superconducting critical temperature and texture

Figure 3-52 shows a graph of onset critical transition temperature ($T_{c,\text{onset}}$) and the transition width (ΔT_c) of six different samples, three samples each from two different precursor flows with same height of laminar flow channels in the A-MOCVD reactor. $T_{c,\text{onset}}$ was determined as the temperature at 90% of the maximum induced voltage of the pick-up coil and $\Delta T_c = T_c^{90\%} - T_c^{10\%}$ after normalizing the pick-up voltage of the coil. Samples grown with 1X flow in A-MOCVD show consistent $T_{c,\text{onset}}$ in a very narrow range of 92.6 K – 92.8 K and ΔT_c of ~ 0.92 K. Samples grown in A-MOCVD with 0.5X flow and 45% conversion efficiency, show even higher T_c onset at 93.1 K -93.4 K and lower ΔT_c of ~ 0.79 K. The quality of the REBCO film has apparently become better with 0.5X flow. Another noticeable feature is the repeatability and consistency of different samples. This relates well with the relatively high self field J_c at 77 K observed in the samples grown with

0.5X flow as mentioned in section 3.4.1. Increase in T_c onset indicates a likely decrease in c -lattice constant and an increase in charge transfer between CuO_2 planes and CuO chains leading to a rise in carrier concentration [143,144].

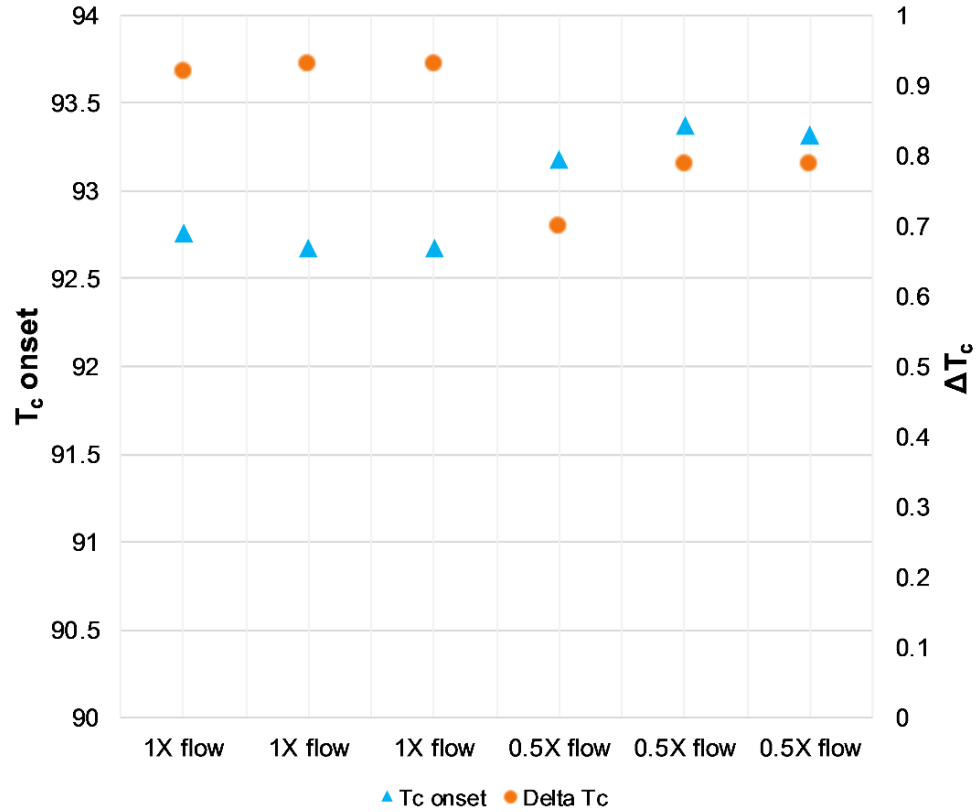


Figure 3-52. $T_{c, \text{onset}}$ and ΔT_c of six different tapes made in A-MOCVD. Three samples were processed with normal (1X) precursor flow and other three with 0.5X flow in a reactor with $\frac{1}{8}$ " channel height.

The out-of-plane texture of 5 mol% Zr doped (Gd, Y)BCO grown with 1X and 0.5X flow using A-MOCVD is depicted in Figure 3-53. The full-width-at-half-maximum (FWHM) values of (Gd, Y)BCO (005) ω -scan grown with 1X flow lies in the range of 1.1-1.25° while FWHM of (005) peak of films grown with 0.5X flow lies in the range 0.9-1.0°.

This trend is consistent with the better self field J_c and T_c of (Gd,Y)BCO grown with less precursor flow. Improvement in out-of-plane texture indicates better crystallinity of the film.

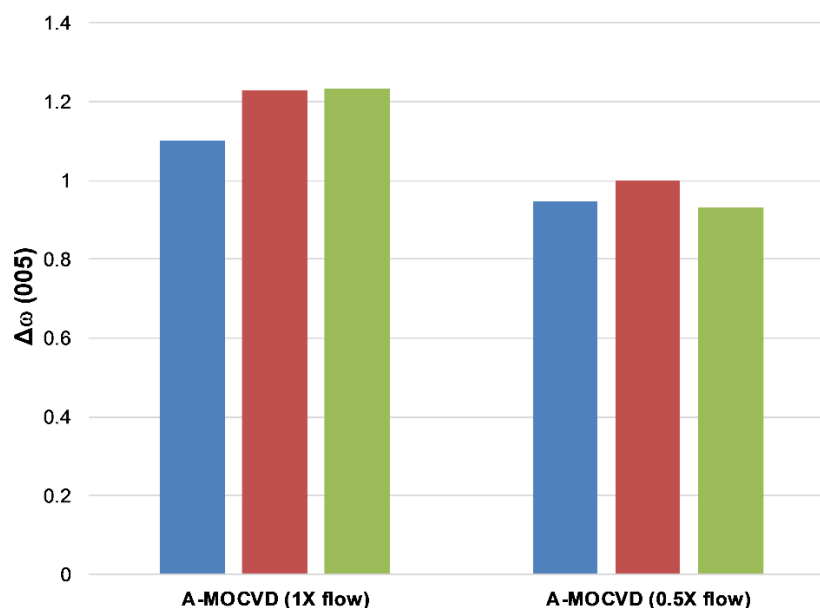


Figure 3-53. Out-of-plane texture (shown in degrees (FWHM) from (Gd,Y)BCO(005) ω -scans of six different samples, three each from A-MOCVD (1X flow - 5% Zr, 0.05 M) and A-MOCVD (0.5X flow - 5% Zr, 0.05 M).

The in-plane texture of 5 mol% Zr doped (Gd, Y)BCO tapes was investigated by XRD ϕ -scan of the (Gd,Y)BCO (103) peak. Figures 3-54(a) and (b) show (Gd, Y)BCO (103) pole figures for tape grown in A-MOCVD with 1X flow and 0.5X flow respectively. Both ϕ -scans show very sharp 103 peaks with similar texture. Figure 3-55 depicts full-width-at-half-maximum values of (Gd,Y)BCO (103) ϕ -scans for six different samples, three each from two different precursor flows with same $\frac{1}{8}$ inch laminar flow channel and same dopant concentration (5 mol% Zr, 0.05 M) in the A-MOCVD reactor. The in-plane texture spread as determined by the FWHM of the (103) peak of all samples lies in the

range $1.9\text{--}2.4^\circ$, films grown with 0.5 X flow showing slightly better in-plane texture. The sharpness of the in-plane and out-of-plane texture of $4.5\text{+ }\mu\text{m}$ thick (Gd, Y)BCO films is very much comparable with the features of thin REBCO films, which proves the control and capability of A-MOCVD to grow high-performance high quality (Gd, Y)BCO films. Such sharp and better in-plane and out-of-plane textures indicate that there has been an improvement in crystallinity with 0.5X flow. As a result, T_c onset has increased and self field J_c at 77 K has also improved.

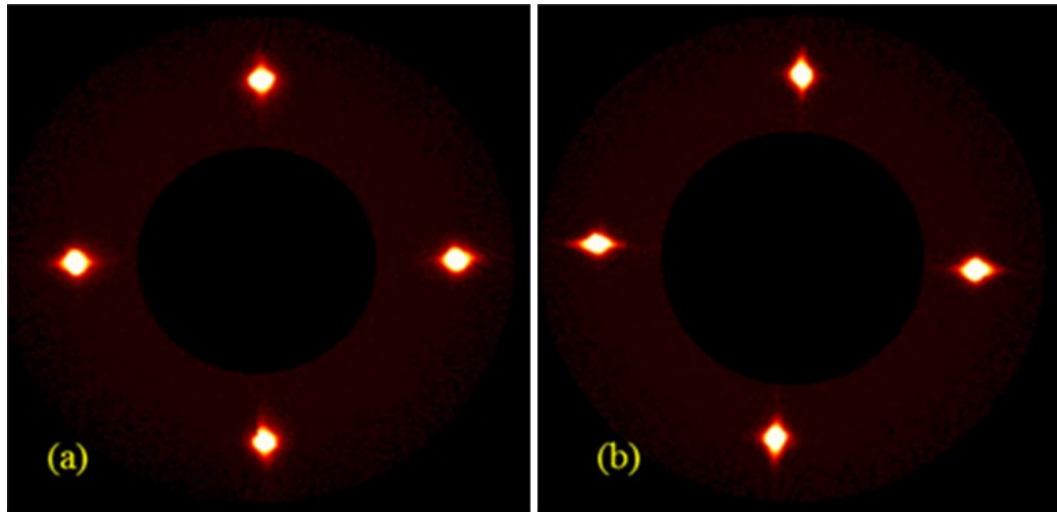


Figure 3-54. (a) and (b) represents (Gd,Y)BCO (103) XRD pole figure of a $3\text{ }\mu\text{m}$ sample deposited with 1X flow and a $4.9\text{ }\mu\text{m}$ sample deposited with 0.5X flow respectively in A-MOCVD, using 5% Zr, 0.05 M precursor.

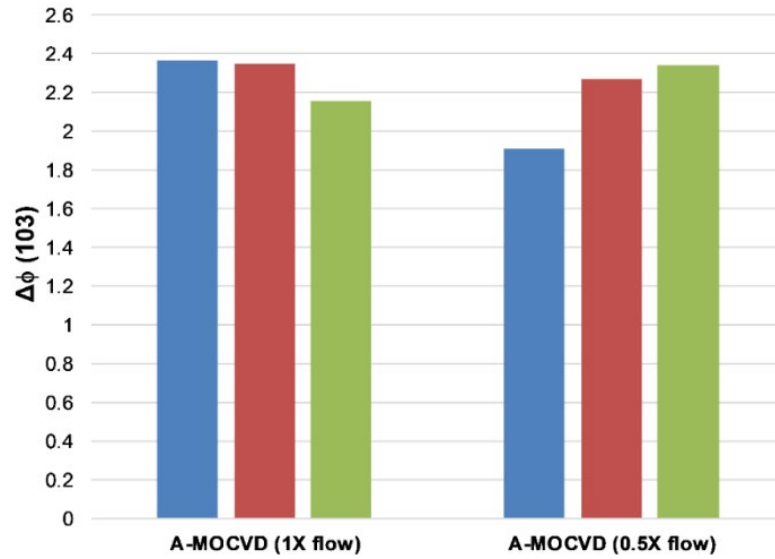


Figure 3-55. In-plane texture (shown in degrees (FWHM) from (Gd,Y)BCO (103) ϕ -scan of six different samples, three each from A-MOCVD (1X flow - 5% Zr, 0.05 M) and A-MOCVD (0.5X flow - 5% Zr, 0.05 M).

3.4.3. Summary

A precursor-to-film-conversion efficiency of ~45% has been achieved in the growth of 4+ μm thick 5 mol.% Zr-doped (Gd, Y)BaCuO tapes using an 1/8" laminar flow channel and half of normal precursor flow. This corresponds to 4X increase in precursor-to-film conversion efficiency compared to that with conventional MOCVD. All thick film REBCO tapes made with A-MOCVD samples exhibit excellent in-plane and out-of-plane texture, high critical temperature (T_c) and narrow transition width (ΔT_c). These results are remarkable in that 4+ μm thick doped (Gd,Y)BaCuO films can be grown at double deposition rate and a 4X precursor-to film conversion efficiency with excellent critical current performance. These advances with A-MOCVD will help reduce 2G-HTS production cost substantially and lead to commercial viability.

Chapter 4. Conclusions and future work.

4.1. Conclusion

An advanced MOCVD reactor has been used to grow thick ($3.5 - 5 \mu\text{m}$) doped and undoped REBCO films with high performance over a wide range of temperature ($77 - 4.2 \text{ K}$) and magnetic fields ($0 - 15 \text{ T}$). A detailed study has been done to check the effect of increasing thickness on the electromagnetic and microstructural properties of REBCO grown using A-MOCVD. In another two separate studies, detailed investigation has been done to optimize composition for high temperature ($77 - 65 \text{ K}$), low field applications ($0.25 - 1.5 \text{ T}$) and low temperature ($50 - 4.2 \text{ K}$), medium to high field applications ($3 - 15 \text{ T}$). Furthermore, another study has been conducted in order to achieve high precursor-to-film conversion efficiency in growing thick REBCO films, without degrading their microstructure and transport self field critical current.

To check the effect of thickness, 5 mol% Zr-doped (Gd, Y)BCO films with thicknesses ranging from 1.1 to $4.8 \mu\text{m}$ have been grown using A-MOCVD. A consistent J_c independent of thickness has been attained in the range of $1.3 - 2.0 \text{ MA/cm}^2$ at 77 K , 0 T . Excellent in-plane texture below 3.5° and out-of-plane texture below 1.5° with high onset critical temperature ($T_{c,\text{onset}}$) in the range of $90.2 - 91.7 \text{ K}$ and transition width (ΔT_c) below 1.1 K have been shown for eleven different films with thicknesses in the range of 1.1 to $4.8 \mu\text{m}$. At high temperature (65 K) and low temperature (30 K), in a magnetic field of up to 9 T ($B \parallel c$), no sign of any degradation has been seen for thicker ($4.8 \mu\text{m}$) film in comparison with thin ($1.1 \mu\text{m}$) film. A very high J_c of 3 MA/cm^2 and pinning force (F_p) of

87 GN/m³ have been shown for 4.8 μ m thick 5 mol% Zr-doped (Gd, Y)BCO tapes at 65 K, 1.5 T (B $\parallel$ c), which exceeds the performance of its 1.1 μ m counterpart.

In order to optimize composition for high performance at high temperature (77 – 65 K) and low magnetic fields, different dopant concentration were investigated. This revealed that undoped (Gd, Y)BCO has the highest self-field J_c at 77 and 65 K and can be used for applications at 77 K and fields lower than 0.2 T. For 0.2 – 5 T, 5 mol% Zr-doped (Gd, Y)BCO films shows higher J_c while above 5 T, 15 mol% Zr-doped (Gd, Y)BCO films dominates and shows better J_c and high retention factor. At 65 K, 1.5 T (B $\parallel$ c -axis) 5 mol% Zr-doped (Gd, Y)BCO films shows record high critical current (1440 A/cm) but with a high anisotropy ratio of 8 due to the presence of long and continuous nanocolumns grown along the c -axis. To reduce anisotropy without degrading critical current in B $\parallel$ c -axis by much, three different studies based on the effect of molarity, different dopant (e.g., Hf), and higher rare-earth content were performed. Increase in deposition rate (with increasing molarity) doesn't seem to attain the desired goal of lower anisotropy. In contrast, it actually degrades the performance with the increased growth of a -axis-oriented grains caused by the increase in surface roughness with an increased deposition rate. Hf dopants at the low concentration of 5 mol% and less Ba (Ba - 1.87 and 1.92) in the compositional ratio tend to form more RE₂O₃ precipitates, which tend to improve self-field J_c and min. J_c at 65 K, 1.5 T and 0.25 T reducing anisotropy by over two-fold and making it more isotropic. 5 mol% Hf-doped (Gd, Y)BCO with a precursor compositional ratio of Y_{0.65}Gd_{0.65}Ba_{1.87}Cu_{2.60}Hf_{0.05} was used to reach over 1440 A/cm at 65 K, 1.5 T (B $\parallel$ c -axis) and a minimum I_c of 1740 A/cm at 65 K, 0.25 T. To further reduce anisotropy, study was conducted on increasing rare-earth content from (Y+Gd-1.3) to (Y+Gd-1.5) in both Zr-

doped as well as Hf-doped (Gd, Y)BCO films. Both Zr-doped and Hf-doped films with Y+Gd-1.5 led to very low anisotropy ratios of 1.1-1.3 at 65 K, 0.25 T, with Hf-doped films dominating in absolute values. $\text{Y}_{0.75}\text{Gd}_{0.75}\text{Ba}_{1.92}\text{Cu}_{2.60}\text{Hf}_{0.05}$ films show a high minimum J_c of 1846 A/cm at 65 K, 0.25 T. Hf-doped films with composition $\text{Y}_{0.65}\text{Gd}_{0.65}\text{Ba}_{1.87}\text{Cu}_{2.60}\text{Hf}_{0.05}$ and $\text{Y}_{0.75}\text{Gd}_{0.75}\text{Ba}_{1.92}\text{Cu}_{2.60}\text{Hf}_{0.05}$ shows much better performance in terms of absolute values and less anisotropy at 65 K, 0.25 and 1.5 T, hence these are better options for application in this regime.

Another study was conducted to achieve high critical current performance in thick (3.8 μm and above) (Gd, Y)BCO films at low temperatures (30 - 4.2 K) in magnetic field range of (3-15 T). This study revealed the best performance in tapes with high dopant concentration (15 mol%) at all fields above 2.5 T. 15 mol% Zr-doped (Gd, Y)BCO shows ~ 1.7 times and ~ 5 times higher J_c than 5 mol% Zr-doped (Gd, Y)BCO and undoped (Gd, Y)BCO respectively at both 30 and 4.2 K in a magnetic field of 13 T ($B \perp$ tape). Further, the effect of different barium concentration with two different dopants (zirconium and hafnium) at a constant high dopant concentration (15 mol%) was analyzed. It was discovered that varying barium in compositional ratio in 15 mol% Zr-doped (Gd, Y)BCO does affect its microstructure and electromagnetic properties while in 15 mol% Hf-doped (Gd, Y)BCO, microstructural properties remains constant. Hf-doped films shows better crystallinity and do not form a -axis oriented grains with lower (Ba-Hf)/Cu, which is in contrast with 15 mol% Zr-doped (Gd, Y)BCO films. In 15 mol% Zr-doped (Gd, Y)BCO films, 77 K self-field J_c peaks at Ba-2.10 while at 4.2 K, 13 T ($B \perp$ tape), Ba-2.15 in 15 mol% Zr-doped (Gd, Y)BCO shows the highest J_c of $\sim 7 \text{ MA/cm}^2$. This is due to the

formation of continuous nanocolumns and increase in its density with increase in barium (from Ba-2.0 till 2.15). Hf-doped films show a decrease in 77 K self-field J_c with increasing barium but at 4.2 K, 13 T ($B \perp$ tape), exhibits a similar $J_c \sim 4\text{-}4.8 \text{ MA/cm}^2$. Generally, comparing 15 mol% Hf-doped and 15 mol% Zr-doped (Gd, Y)BCO films with different barium content, Hf-doped films with same (Ba-M)/Cu ~ 0.70 perform better at 77 K self-field (17 % higher J_c than Zr-doped (Gd, Y)BCO films) while the 15 mol% Zr-doped film exhibits 32 % higher J_c at 4.2 K, 13 T ($B \perp$ tape).

A 4.8 μm thick, 15 mol% Zr-doped (Gd, Y)BCO tape showed record-high critical currents of 8705 A/12 mm, 5586 A/12 mm and 3606 A/12 mm at 30 K, 40 K and 50 K respectively in a magnetic field of 3 T ($B \parallel c\text{-axis}$) which are approximately two times higher than the best values reported in literature. Engineering critical current density (J_e) of this tape at 40 K, 3 T is more than 7 times higher than that of the best commercial HTS tapes.

Critical currents of two different 4+ μm thick, 15 mol% Zr-doped (Gd,Y)BaCuO tapes were measured at low temperature and high fields at LBNL and NHMFL. Remarkably, high critical currents of 2247 A/4 mm and 2119 A/4 mm have been obtained at 4.2 K, in a magnetic field of 14 T ($B \parallel c\text{-axis}$), which are approximately a factor of two higher than the best values reported in the literature. High critical current density of over 12 MA/cm^2 and pinning force of 1.7 TN/m^3 have been achieved. An engineering current density (J_e) (considering a typical 40 μm thick copper stabilizer) of over 5 kA/mm^2 has been achieved at 4.2 K, 14 T ($B \parallel c\text{-axis}$) which is more than five times higher than that

of Nb₃Sn and nearly four times higher than the highest reported value of all superconductors other than REBCO at this field and temperature.

In a separate study, a precursor-to-film-conversion efficiency of ~45% has been achieved in the growth of 4+ μm thick 5 mol.% Zr-doped (Gd, Y)BaCuO tapes using an $\frac{1}{8}$ " laminar flow channel and half of normal precursor flow. This corresponds to 4X increase in precursor-to-film conversion efficiency compared to that with conventional MOCVD. All thick film REBCO tapes made with A-MOCVD samples exhibit excellent in-plane and out-of-plane texture, high critical temperature (T_c) and narrow transition width (ΔT_c). These advances with A-MOCVD will help reduce 2G-HTS production cost substantially and lead to commercial viability.

4.2. Future works

Results shown in this work are just a step forward in realizing the potential of thick REBCO films. Several different ideas may be considered to further investigate the properties of these thick films, which are described as follows:

- (1) Long length thick REBCO:** For the present study, 32 cm length samples were deposited in stationary condition and short sections were used for different characterization studies. It is necessary to increase the length of these thick REBCO films to at least 50 m for any commercial applications. Necessary hardware changes and process parameter optimization need to be developed.
- (2) Improving precursor-to-film conversion efficiency:** As shown in the present result, this method is another way forward in reducing the cost of REBCO.

Reducing channel height and varying flow and molarity accordingly can improve the efficiency further. Also, attaining a lower deposition pressure with hardware change can improve the deposition rate and hence increase the conversion efficiency. Another possibility is changing the hardware to have lateral flow of precursor along the tape length to increase conversion efficiency further.

(3) Different buffers: For the current study, only IBAD MgO with LaMnO₃ as cap layer has been used. Different buffers stack with improved in-plane and out-plane texture can be considered to further improve the critical current density of thick REBCO. Also, different types of buffer such as YSZ stacked – IBAD MgO/ IBAD LMO should be considered for applications where a metal substrate is not a viable option. Some experiments have been tried in this regard, which has not been presented in this thesis, but can serve as a background information.

(4) High dopant concentration: More than 15 % dopant concentration should be considered with different dopants (Zr , Hf) to further improve the in-field properties at lower temperature.

(5) Optimizing rare-earth ratios: In the current research, yttrium and gadolinium has been used in 1:1 ratios. It has been observed that most of RE₂O₃ precipitates comes from Y₂O₃. As we have seen the impact of these precipitates on electromagnetic and microstructural properties, its worth optimizing different ratios to control the RE₂O₃ precipitates and achieve the desired result. Initial results have been tried, which are not presented here, that can serve as a background information.

(6) Effect of barium : In the current study, effect of different barium concentration has been done on 15 mol% Hf doped (Gd, Y)BCO and 15 mol% Zr-doped (Gd,

Y)BCO. Several results are still not clear in this study which need to be understood.

This study can be extended to lower dopant concentration and even higher dopant concentration.

(7) Different dopants: Several other dopants like niobium, cerium, terbium etc can be tried to investigate their impact on thick REBCO films.

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