

Study of Structure, Composition and Electromagnetic Properties of High Levels of
Zr-Doped $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ Tapes Fabricated by Metal Organic Chemical Vapor Deposition

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Yuhao Liu

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Abstract

In this thesis the critical currents (I_c), structural properties and composition variations of Zr-doped (Gd,Y)Ba₂Cu₃O_x (GdYBCO) superconducting tapes fabricated by metal organic chemical vapor deposition (MOCVD) were studied. By a modified MOCVD process, the self-field critical currents at 77K of GdYBCO with high Zr doping levels have been enhanced significantly. The in-field performances of critical currents of GdYBCO tapes with Zr-doping levels of 7.5-30 at.% were investigated up to 5 T over a temperature range of 40 K – 77 K. The tape with 20% Zr doping is found to have the highest minimum critical currents and the highest critical currents in orientation of the field perpendicular to the c-axis ($H \parallel c$) over a wide range of temperatures and magnetic fields. The electromagnetic properties have been related to the microstructure changes. For finding out the optimal film composition with the best in-field performance at 30K, 3T, the influence of composition on in-field performance has also been studied.

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Chapter 1 Introduction

1.1 Introduction of superconductivity

In 1908, Kamerlingh Onnes and his colleagues in the Netherlands realized the liquefaction of helium, which opened a new field of extremely low temperatures. In 1911, they discovered that the electrical resistance of pure mercury disappeared suddenly at liquid-helium temperatures. Onnes found that the induced current in a superconducting ring did not decay over time which verified that electrical resistance of the superconductive state was in fact zero [1].

In 1933, Walther Meissner and Robert Ochsenfeld measured flux distributions of Sn and Pb as they were cooled down below a transition temperature in an applied magnetic field [2]. It was found that the superconductive sample expelled all magnetic flux, which was another important aspect of superconductivity. It was called the Meissner effect.

The Meissner effect is caused by induced currents at the surface of the superconductor. These surface currents could generate additional magnetic fields to cancel the applied magnetic field within the bulk of the superconductor. The screening currents exist in a surface layer with a very small thickness, leading to the fact that the flux density caused by the applied magnetic field could not decrease suddenly but gradually — the London penetration depth was described by brothers Fritz and Heinz London in 1935 [3]. In 1950, the Ginzberg–Landau (GL)

theory was put forth by Landau and his colleagues [4], which is a macroscopic phenomenological model used to describe superconductivity. In 1957, John Bardeen, Leon Neil Cooper, and John Robert Schrieffer proposed the Bardeen–Cooper–Schrieffer (BCS) theory [5], which explained the microscopic mechanism of superconductivity for the first time since the discovery of superconductivity in 1911. After the BCS theory, in 1957 Lev Gor'kov proposed the Abrikosov–Gorkov (AG) theory as a bridge between the macroscopic GL theory and the microscopic BCS theory, showing a consistent theoretical framework.

1.2 Introduction of superconductors

After Onnes discovered the superconductivity in pure mercury in 1911, superconductivity in metal elements was investigated first. The element with the highest critical temperature is Nb, transforming to the superconductive state at 9K. After the highest critical temperature of superconductors was raised to 15K by the discovery of NbN in 1941, Nb-based compounds were found with high critical temperatures. Nb₃Sn was discovered to be a superconductor with a critical temperature of 18.3K in 1954 [6]. It was discovered that Nb₃Sn could maintain superconductivity with large currents and strong magnetic fields [7], which is essential for manufacturing high-field magnets. However, it was difficult to wind Nb₃Sn into coils because of its poor mechanical properties. In 1962, a NbTi superconductor was developed by researchers at Westinghouse, with a critical temperature of 9.2 K and a critical magnetic field of 15T. Although its critical magnetic field is lower than that of Nb₃Sn, the electromagnetic property of NbTi is

still sufficient for most applications with a relatively low operation magnetic field. Since NbTi is ductile and can be processed into wires by extrusion and drawing, it is widely used in almost all superconducting magnets of 5T or lower.

In 1986, Bednorz and Muller discovered superconductivity in La-Ba-Cu-O system with a critical temperature of 35 K, which is above the upper limit 30K predicted by the previous BCS theory [8]. The discovery of LBCO stimulated researchers' interest in new materials with similar structures and started a new field of high- T_c superconductivity. In 1987, Wu and Chu discovered a superconductive compound known as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (T_c of 93K) [9]. With this compound, the critical temperature of superconductors rose above the boiling point of liquid nitrogen, leading to a significant decrease in the cost of cooling. In 1988, Maeda discovered $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$ as a superconductor with the critical temperature of 107K, which is the first high-temperature superconductor containing no rare-earth elements [10].

1.3 Applications of superconductors

Superconductors can transport much larger currents than ordinary copper and aluminum wires, so superconducting magnets can produce greater magnetic fields than the best electromagnets made by normal conductors. Superconducting materials for actual applications can be sorted into two categories: low-temperature superconductors (LTS) such as NbTi and Nb_3Sn with operation temperatures of around 4.2 K and high-temperature superconductors (HTS), including $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Bi-2223) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO), which can operate at temperatures up to the boiling point of liquid nitrogen (77K).

All the above superconductors are Type II superconductors, with an upper critical field. However, for HTS materials (Bi-2223 and YBCO), a lower characteristic field called “irreversibility field” is more meaningful for actual applications. In Fig. 1-1, the upper critical fields of Nb47wt.%Ti, Nb₃Sn and the irreversibility fields of Bi-2223 and YBCO are shown.

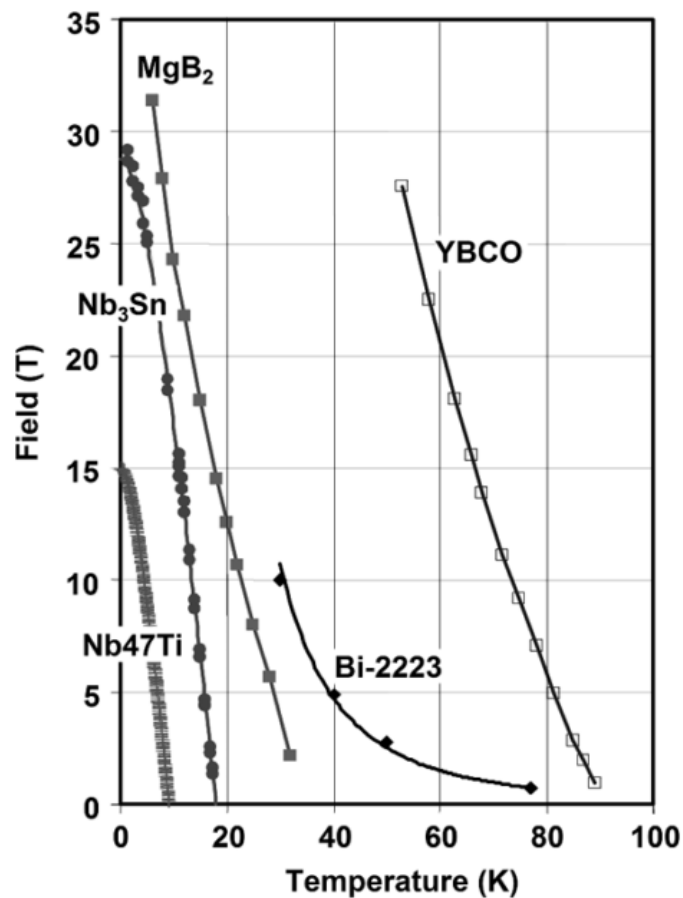


Fig. 1-1 Upper critical fields of Nb47wt.%Ti, Nb₃Sn and Irreversibility fields of Bi-2223 and YBCO [11].

1.3.1 Applications of low-temperature superconductors

During the 1980s, the manufacturing processes of low-temperature superconductors NbTi and Nb₃Sn were commercially optimized based on a detailed

scientific understanding. Nb-based superconducting wires have been applied in applications requiring high magnetic fields such as Magnetic Resonance Imaging (MRI) in medicine, Nuclear Magnetic Resonance Spectroscopy (NMR) in biology and chemistry, magnets for Nuclear fusion power technology and magnets for particle accelerators in High Energy Physics [12].

Magnetic Resonance Imaging (MRI) for medical diagnostic requires a magnetic field with uniform field density and strength. The field density in a MRI cannot vary more than 1 ppm/h, and the typical field level of a whole body scanner is usually between 1.5T and 3T. Now functional MRI (fMRI) has been developed to achieve fast acquisition of images which need higher fields from 3T to 4T [12]. MRI has non-ionizing electromagnetic fields, which are totally harmless to the patients, unlike CT scans and traditional X-rays.

Nuclear Magnetic Resonance (NMR) spectroscopy, is a powerful analytical tool in chemistry, biology, medicine and materials research. In NMR spectroscopy the magnetic resonance is utilized to show molecule structural information. As the spectroscopic resolution of NMR increases with the magnetic field, a higher magnetic field is desirable. The magnetic field level of commercial NMR spectrometers varies from 7T for standard industrial applications to 23T for high resolution spectroscopy. The magnets below 9.4T are made up only of NbTi conductors, and the magnets above 11.8T are mainly built with Nb₃Sn conductors [12].

Nuclear fusion could be a future source of electrical energy. The primary energy comes from the collision of hydrogen nuclei and the formation of helium nuclei like the nuclear fusion reaction that happens in the sun. Two fusion devices are specialized to achieve nuclear fusion reaction — the TOKAMAK and the STELLARATOR. The magnetic fields of the TOKAMAK range from 12T to 13T and the STELLARATOR needs lower fields of about 6T [12].

Superconductors are widely applied in accelerator technology for high energy physics as beam line magnets and detector magnets. Several large superconducting accelerators were constructed and operated successfully, such as the Large Hadron Collider (LHC) in Geneva, Switzerland [12].

1.3.2 Applications of high-temperature superconductors

The discovery of High-Temperature Superconductor (HTS) in 1986 by Bednorz and Muller expanded the applications of superconductors since liquid nitrogen could be utilized as a cryogenic environment with a lower cost than helium cooling. HTS conductors for practical applications are mainly based on Bi-2223 ($\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$), known as a first generation HTS conductor, and REBCO ($\text{REBa}_2\text{Cu}_3\text{O}_x$) — a second generation HTS conductor, where RE stands for rare earth and YBCO is the best-known example.

Bi-2223 was the first commercial HTS superconductor, consisting of multi-filaments of the superconductor in a silver matrix, which sets a lower limit as to how inexpensive the conductors can be. As shown in Figure 1-1, Bi-2223 has a lower

irreversibility field compared with YBCO; for example, it can lose superconductivity in a low magnetic field 0.2T at 77K.

Since REBCO conductors use much lower amounts of silver than Bi-2223, REBCO conductors have the potential of costing less, and could also carry higher current densities at high magnetic fields and high temperatures. So far, HTS conductors have been developed and utilized in power cables, transformers, coils of generators and motors, etc.

Power cables. HTS power cables have large power capacity, low power transmission losses and are compact. HTS power cables can carry about five times the current of a normal copper cable with the same diameter. Although the extra power for cooling could decrease the overall efficiency, superconductor power cables still have a much higher overall efficiency than any other long-distance transmission system [13]. Figure 1-2 shows the structure of 3-in-one HTS cables developed by Sumitomo Electric Industries, which has been applied in an actual power grid of National Grid Company in Albany, NY [14]. The initial power cable was made of Bi-2223 tapes. After long-term testing in 2008, 30m cables using YBCO tapes produced by SuperPower were installed to replace a segment of the original 1G HTS cable [15].

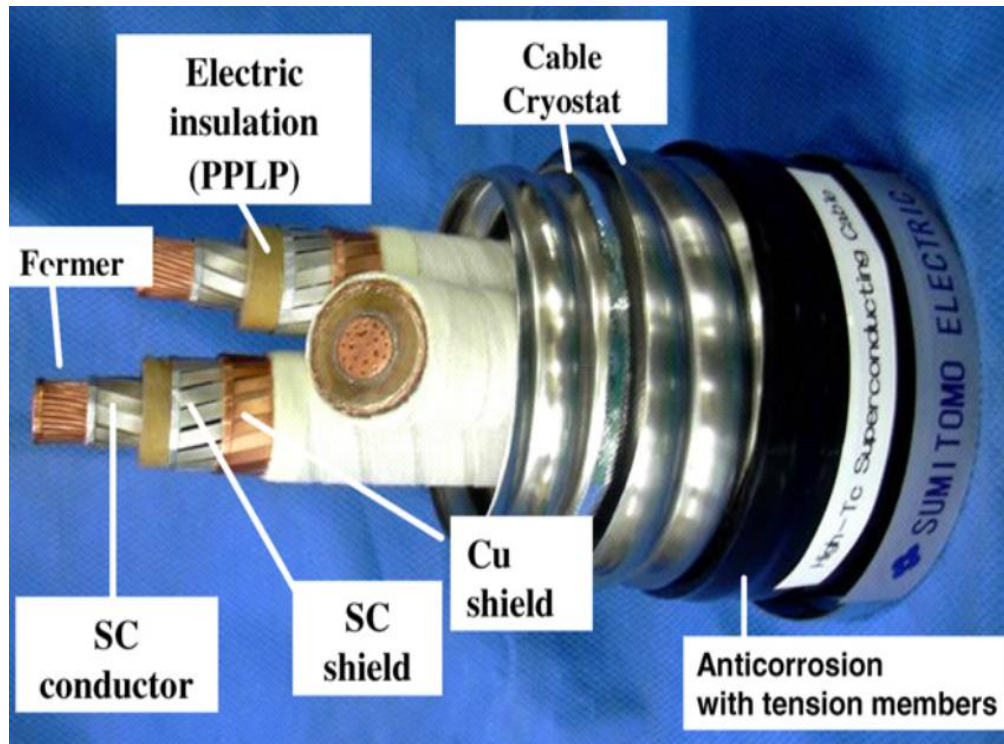


Fig. 1-2 Structure of 3-in-one HTS power cable.

Motors. HTS motors could realize a 50% reduction in both weight and size compared to conventional motors of the same rating. Smaller sizes could lead to the reduction of friction and windage loss. The first generation high-temperature superconductor (1G HTS) wires have been used to demonstrate large-scale prototype devices, such as a 400kW feasibility demonstration motor [16], a 5 MW U. S. Navy motor, an 8 MW synchronous condenser and a 36.5 MW motor [17]. Considering the lower cost potential of 2G HTS wire, 2G HTS motors such as the 15kW synchronous motor using YBCO tapes in Japan [18], have been investigated and developed as shown in Figure 1-3.



Fig. 1-3 15 kW synchronous motor using YBCO tapes [18].

Wind generators. At present, the wind industry has started to develop offshore wind turbines since higher wind speeds are available offshore compared with on land. In order to decrease the cost of construction, maintenance and transportation in offshore wind power, turbines with high power ratings of 10 MW and above are preferred [19]. For high power-rating wind turbines, failure of gearboxes caused by high rotational speeds become a significant issue. By connecting turbine blades without a gearbox, direct drive superconducting generators could provide a compact and light weight drive train at high torques and slow rotational speeds. AMSC has designed a 10 MW wind turbine based on the 1G HTS generator (Bi-2223) with the brand name SeaTitan [20], as shown in Figure 1-4.

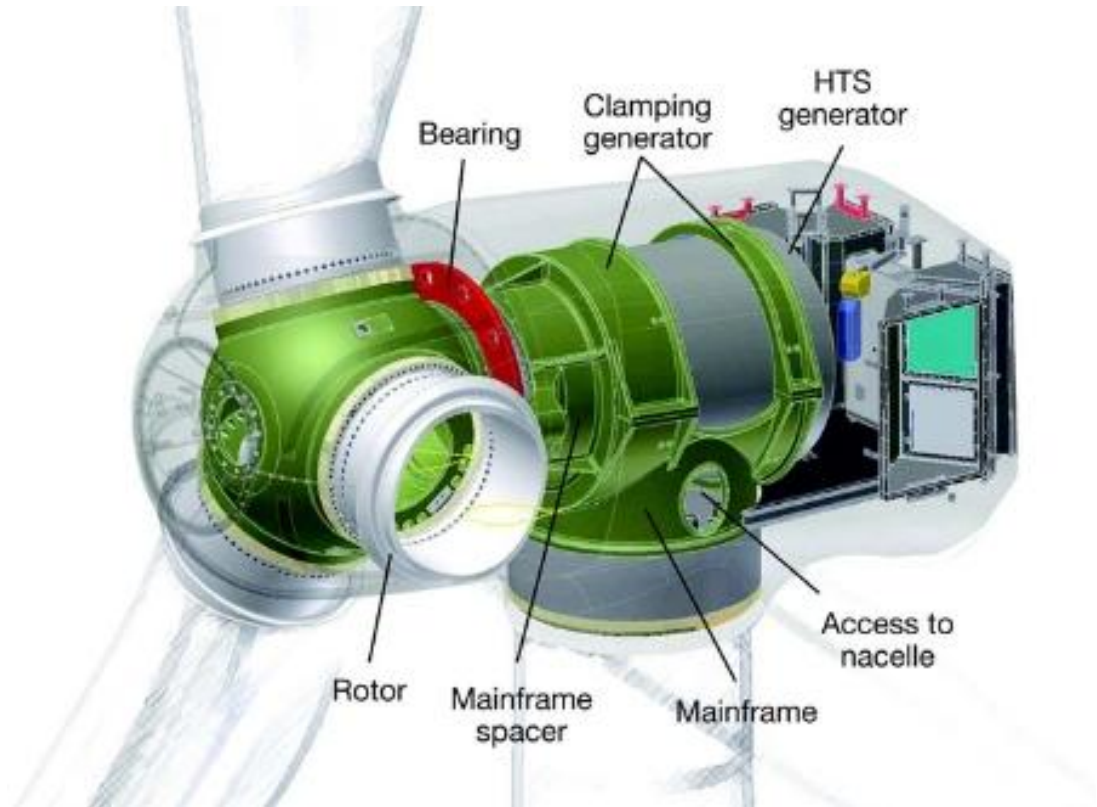


Fig. 1-4 Schematic figure of 10MW direct drive superconducting wind turbine [20].

Beginning in 2012, our group started to focus on enhancing the in-field performance of a 2G HTS superconductor at 30 K, 2.5 T for the 10 MW wind generators collaborating with SuperPower, Tai-Yang Research, TECO-Westinghouse and National Renewable Energy Laboratory.

1.4 2G HTS conductor

1.4.1 Basic information of 2G HTS conductors

As mentioned before, compared with other commercial superconductors REBCO has the potential of low cost and excellent current capability at high magnetic fields and high temperatures. The crystal structure of YBCO is shown in Figure 1-5.

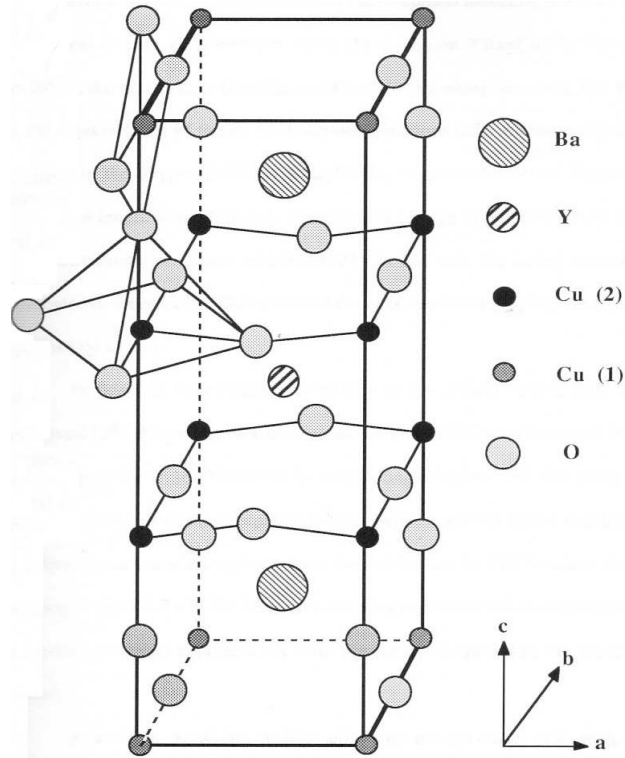


Fig. 1-5 Lattice structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [21].

In the lattice structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$, Cu(1)-O atoms form chains along the b axis and Cu(2)-O atoms form the planar sheet in the a-b plane. Cu(2)-O planes are responsible for the superconductivity of YBCO. It is also found that the oxygen atoms of Cu(1)-O chains along the b axis affect superconductivity properties significantly. If x is equal to 0 in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, it means there are no free oxygen sites in the lattice. The oxygen atoms in the Cu(1)-O chains along the b axis will enlarge the unit cell parameters along the b axis, making the lattice as an orthorhombic structure ($a_0 = 0.382 \text{ nm}$, $b_0 = 0.389 \text{ nm}$, $c_0 = 1.168 \text{ nm}$). When x is equal to 1, all oxygen atoms are removed from the Cu(1)-O chains along the b axis, resulting in a tetragonal structure ($a_0 = b_0 = 0.386 \text{ nm}$, $c_0 = 1.168 \text{ nm}$), with the unit cell parameters along the b axis equal to that along the a axis.

Figure 1-6 shows that superconducting transition temperature T_c of YBCO stays around 90K when x varies from 0 to 0.25, then decreases to around 60K till $x=0.4$. When x is larger than 0.6, the superconducting transition temperature drops to zero, which means YBCO then is no longer a superconductor.

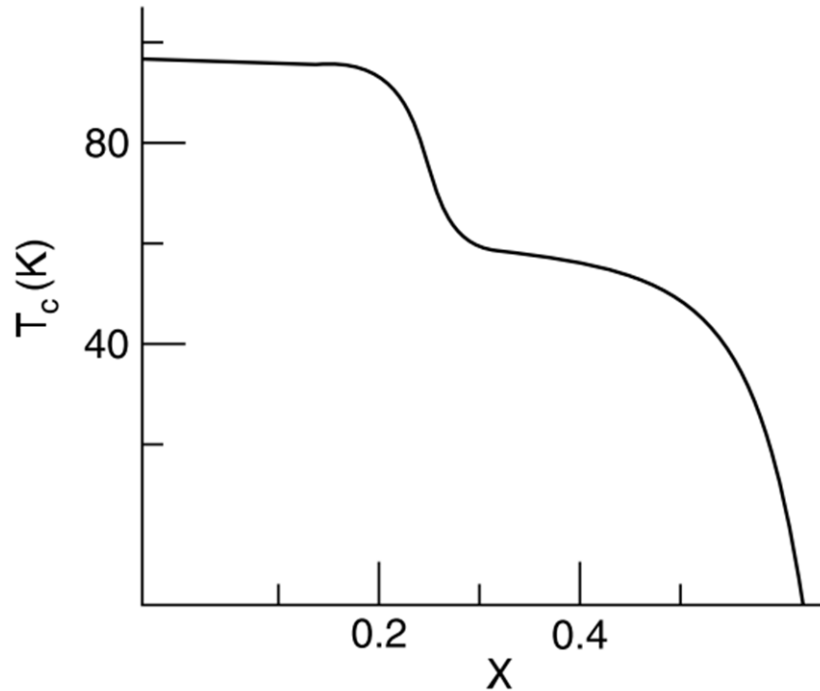


Fig. 1-6 Variation of superconducting transition temperature of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with the oxygen stoichiometry x [21].

1.4.2 Fabrication of 2G HTS conductors

As shown in Figure 1-7, second generation superconductors (coated conductors) consist of four different layers: the metallic substrate usually made of nickel-based alloy, the buffer layer for preventing the diffusion contamination from the substrate to the superconducting layer, the biaxially-aligned YBCO layer and a stabilizing layer.

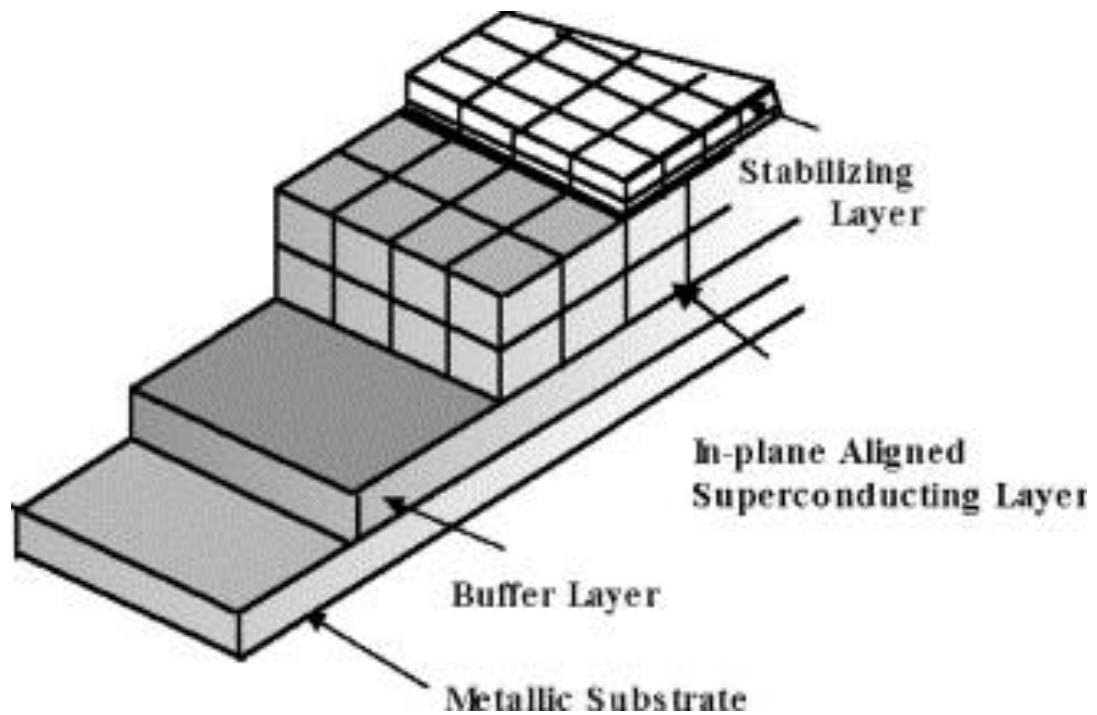


Fig. 1-7 Schematic structure of 2G HTS conductors.

In the early period of YBCO tape fabrication, its critical current density was found to be suppressed by large-angle grain boundaries in ab planes, which is caused by the polycrystalline substrates [22]. For enhancing the current carrying capacity of YBCO film, it was found that it is necessary to achieve biaxial texture in the buffer layer or in the metallic substrate. So far, three technologies have been developed for achieving biaxial texture: Ion Beam Assisted Deposition (IBAD), Rolling Assisted Biaxially Textured Substrates (RABiTS), and Inclined Substrate Deposition (ISD)

Ion Beam Assisted Deposition (IBAD). Biaxially-textured buffer layers are made by the ion beam bombardment deposition with dual ion sources: sputtering ion source and assisting ion source, as shown in Figure 1-8. In 1991, biaxially-oriented buffer layers of yttria stabilized zirconia (YSZ) were demonstrated on polycrystalline,

Ni-based alloy by ion-beam assisted deposition (IBAD) by the Fujikura Company [22]. After depositing YBCO films on the YSZ layers, it was found that the critical current of YBCO based on IBAD technology increased more than twenty times higher than the critical current of YBCO processed by conventional methods on polycrystalline substrates [22]. X-ray pole figure measurement and TEM planar observations both verified that 50% of the grains had misorientation angles of less than five degrees [23]. Usually, a thick film ($> 1 \mu\text{m}$) of YSZ is usually required to achieve a good in-plane alignment, causing a long processing time and higher cost. In 1997, IBAD MgO was developed to substitute YSZ because IBAD processed MgO has better in-plane alignment with a thinner layer.

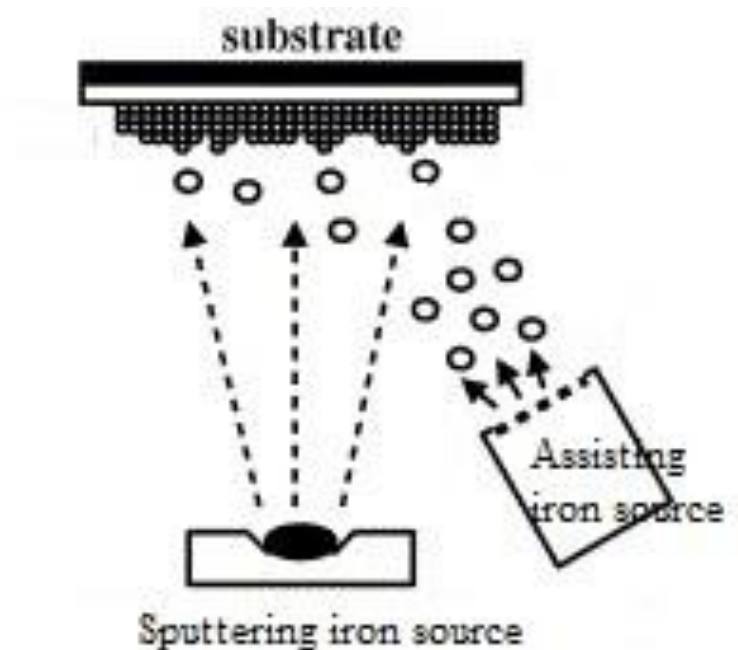


Fig. 1-8 Schematic figure of Ion Beam Assisted Deposition.

Rolling Assisted Biaxially Textured Substrates (RABiTS). The RABiTS technique uses standard thermo-mechanical processing of metals such as Ni to obtain

long lengths of biaxially-oriented substrates with smooth surfaces. This method starts with a randomly-oriented Ni rod that is processed by cold rolling and re-crystallization annealing. The resulting biaxially-oriented substrates provide the required template for the growth of oxide buffer layers and the superconductor [24]. The grain size of RABiTS substrates is very large (~ 50 microns), compared to that of IBAD templates.

Inclined Substrate Deposition (ISD). Without the aid of an assisting ion source like the one in IBAD, a biaxially-textured film of YSZ or MgO can be deposited on an inclined substrate [25]. ISD could achieve a high deposition rate, but the biaxial texture quality and the critical current density of YBCO that are processed after ISD are not good enough. There are many processes for growing high performing YBCO superconductor layers on the biaxial-textured buffer layer, such as pulsed laser deposition (PLD), metal organic deposition (MOD) and metal organic chemical vapor deposition (MOCVD).

Metal Organic Deposition (MOD). Metal organic deposition is a solution-based deposition technique using metal organic precursors. MOD using trifluoroacetate precursors (TFA) has been applied for the fabrication of a high critical density YBCO conductor by the American Superconductor Corporation [26]. As shown in Figure 1-9, first the tape with biaxial-textured buffer layer is processed by a coating process using a trifluoroacetate (TFA)-based precursor with Y, Ba and Cu in a 1: 2: 3 molar ratio. After the coating process, the tape is decomposed into BaF_2 , CuO

and Y_2O_3 at 400 degrees, then converted to epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at 700–800 degrees.

After the oxygenation process, the tape could convert to $\text{YBa}_2\text{Cu}_3\text{O}_7$ completely.

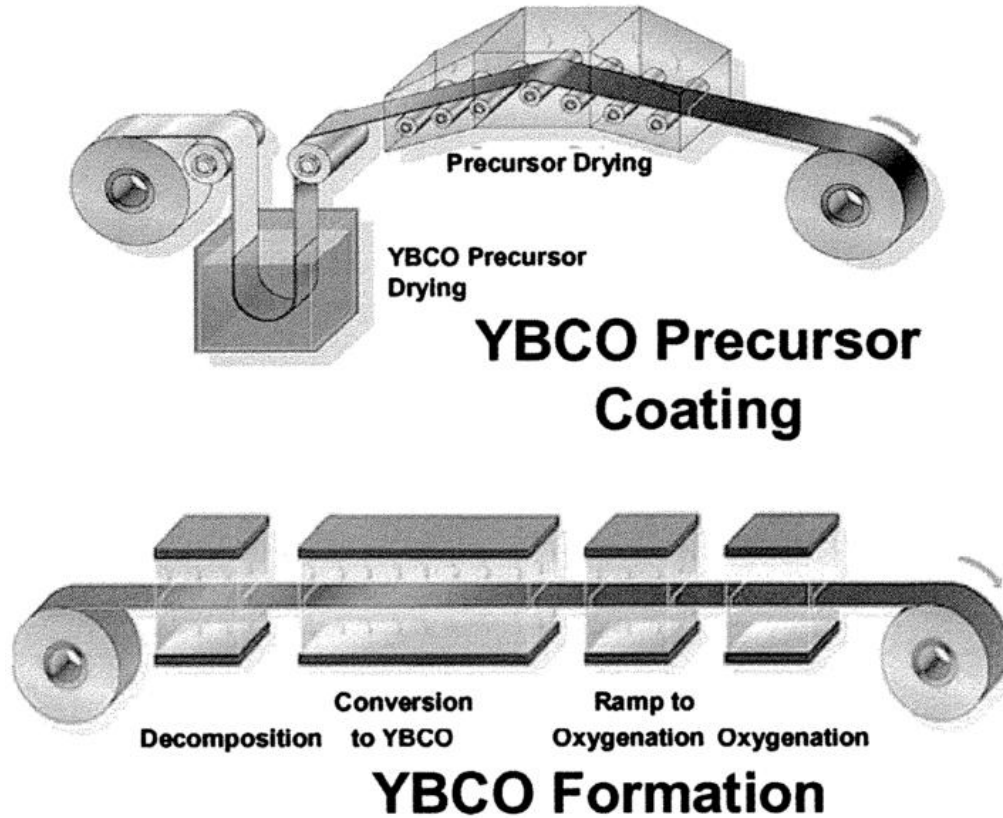


Fig. 1-9 Process of reel-to-reel fabrication of YBCO based on TFA-MOD technology [27].

The American Superconductor Corporation has combined TFA-MOD with RABiTS technology, producing 600 meters of 2G production wire with a $0.8\ \mu\text{m}$ thick YBCO layer which could carry a critical current in the range of 200–275 A/cm-w [26]. The architecture of American Superconductor Corporation's 2G HTS wire is shown in Figure 1-10. Three buffer layers, Y_2O_3 , YSZ and CeO_2 , are deposited on a biaxially-textured nickel alloy followed by MOD of YBCO. Although the MOD process is simple to realize, it has a slow processing rate and difficulties in fabricating thick films.

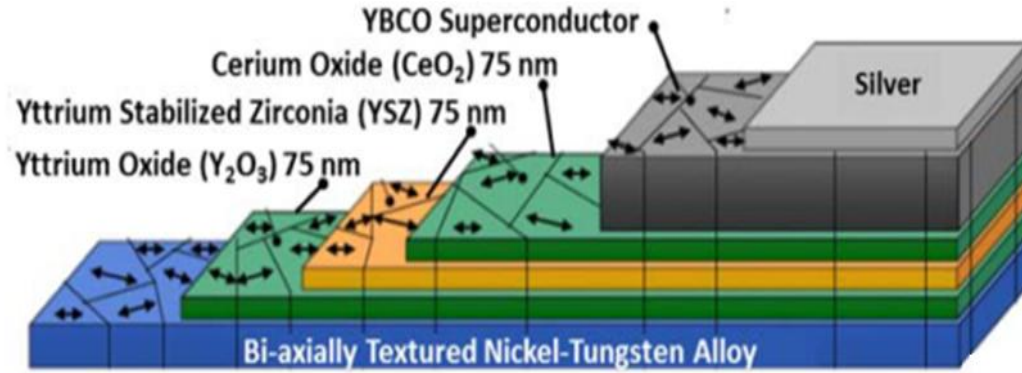


Fig. 1-10 The architecture of American Superconductor Corporation's 2G HTS wire [26].

Metal Organic Chemical Vapor Deposition (MOCVD). Metal organic chemical vapor deposition is a chemical vapor deposition method, widely applied in the semiconductor industry for fabricating epitaxial thin films. In this process, a metal organic vapor with the required chemical elements is injected into a chamber and deposited on a substrate by a chemical reaction. For improving the stability of precursor delivery, flash evaporation of mixed solution of metal organic sources has been developed. A solution of metal organic precursors is exposed to elevated temperatures for a very short time, which is just enough for the evaporation process [28]. The IBAD/MOCVD technique is the main method used to fabricate 2G HTS conductors by Superpower, Inc., which is also the method focused on in this work. The conductor architecture is shown in Figure 1-11. Zero-field critical currents of 803 A/cm have been reported in 12mm wide, 3.5 micrometer thick films [15]. In 2008, a 1030m long conductor with a minimum critical current of 227 A/cm has also been achieved by IBAD/MOCVD [29].

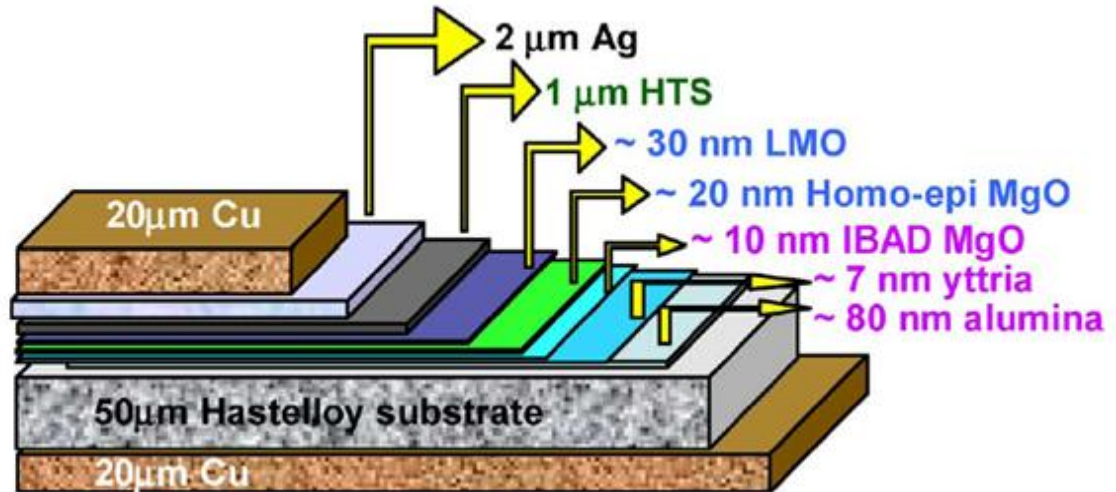


Fig. 1-11 The conductor architecture of 2G HTS fabricated by IBAD/MOCVD by Superpower, Inc.

Although MOCVD has a relatively low precursor conversion efficiency compared with PLD and MOD, it has the fastest deposition process and largest deposition area which are important for low cost and high throughput.

1.4.3 Flux pinning of REBCO

For describing flux pinning properties of REBCO superconductors, two important parameters need to be introduced: penetration depth λ and coherence length ξ . The penetration depth λ describes the penetration distance of the magnetic field into superconductors. The region over the distance λ shows perfect diamagnetism without any flux density. Since the boundary between superconducting and normal regions cannot be perfectly sharp, the coherence length ξ shows the transition distance between superconducting and normal regions. Over the coherence length ξ , the density of superelectrons n_s decreases to zero.

In the Ginzberg–Landau (GL) theory, λ/ξ , called the Ginzburg-Landau constant, which is used for distinguishing Type I superconductor and Type II superconductor. For $\lambda/\xi < 1/\sqrt{2}$, the surface energy of superconductors is positive, which is the characteristic of Type I superconductors. For $\lambda/\xi > 1/\sqrt{2}$, the surface energy is negative, corresponding to Type II superconductors. Considering that the surface energy at the boundary between superconducting and normal states is negative in the Type II superconductor, the formation of boundary surfaces between superconducting and normal states could reduce the free energy. So a large number of normal regions are preferable to form in the superconductors with increasing applied magnetic field. The state of the coexistence of normal state and superconducting state in Type II superconductor is called the mixed state.

Two critical fields are defined in Type II superconductors due to the mixed state: the lower critical field H_{c1} and the upper critical field H_{c2} , separating a superconductor phase diagram into three regions as shown in Figure 1-12. As the magnetic field increases beyond H_{c1} , the superconductor enters into a mixed state with the formation of normal cores. As the field increases beyond H_{c2} , the material totally transfers to the normal state. The existence of an upper critical field in Type II superconductors is the main reason for the fact that Type II superconductors can be utilized at much higher magnetic fields than Type I superconductors.

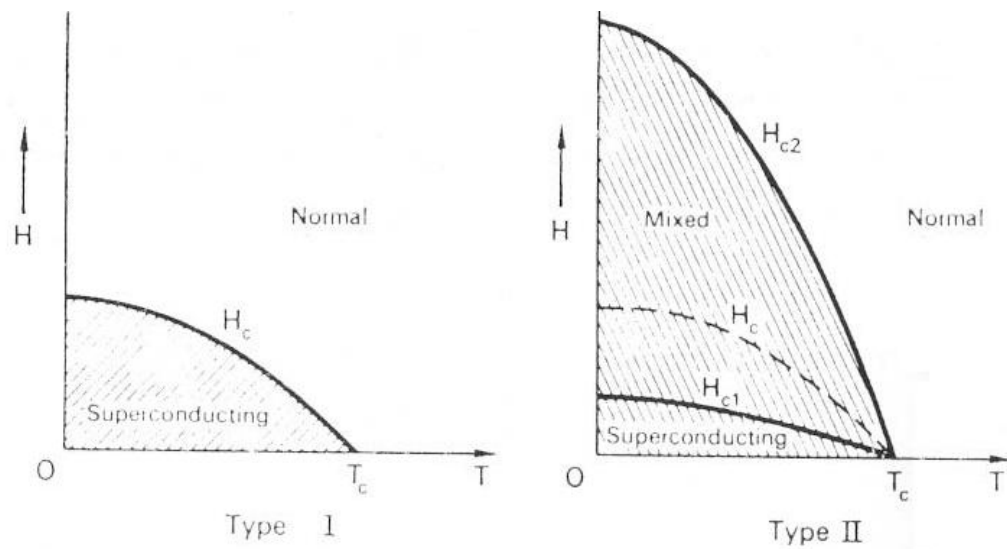


Fig. 1-12 Magnetic field-Temperature Phase diagram of Type I and Type II superconductors [30].

In the mixed state, the normal cores will form along the direction parallel to the applied magnetic field. In each normal core, a magnetic flux passes along the direction of the applied magnetic field, generated by electrical superconducting currents (supercurrents) circulating around the normal core. Because the normal cores repel each other due to the Lorentz force, in an infinitely large, defect-free Type II superconducting material, the cores arrange themselves in a hexagonal periodic lattice, verified by a magnetic decoration technique, as shown in Figure 1-13.

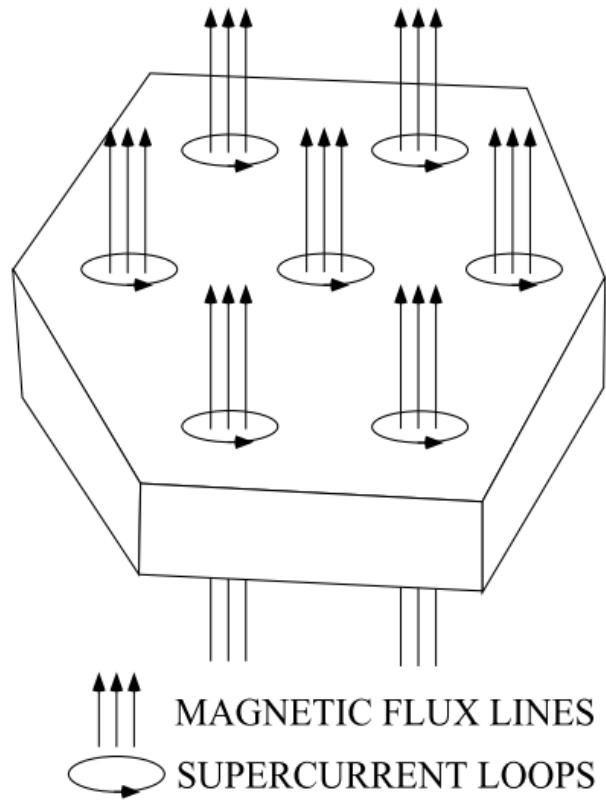


Fig. 1-13 Schematic diagram of flux vortices in a Type II superconductor [31].

A schematic structure of a flux vortex is shown in Figure 1-14. The radius of each cylindrical normal core is characterized by the coherence length ξ , where the density of superelectrons (cooper pairs) n_s decreases to zero at the center.

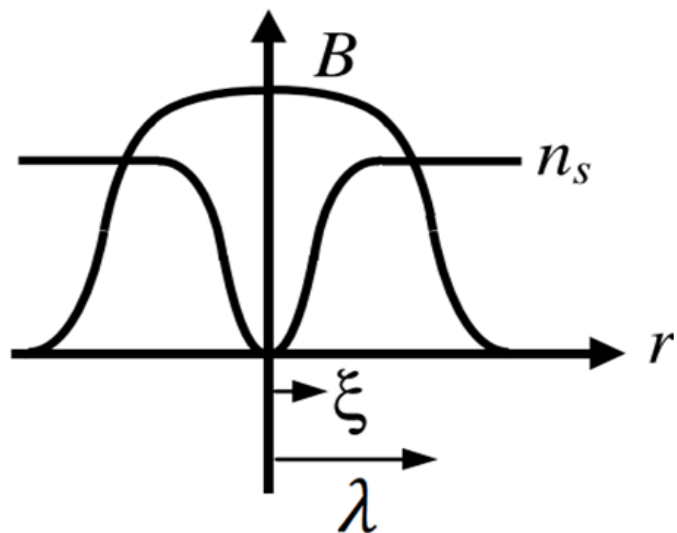


Fig. 1-14 Schematic structure of flux vortex.

The magnetic flux in the normal core falls to zero in the superconducting matrix over a distance λ from the vortex center. The penetration depth λ also shows the characteristic radius of supercurrent loops.

As a Type II superconductor carries external transport currents in the presence of an applied magnetic field, Lorentz forces are induced on the vortices due to the flux in the vortices and the transport current, as shown in Figure 1-15,

$$f_L = J \times \Phi_0, \quad (1-1)$$

where f_L is the Lorentz force per unit length of the vortices, J is the transport current density and Φ_0 is the magnetic flux of each vortex. If vortices are moved by the Lorentz force, then work is done. The dissipated energy leads to an electrical resistance in the sample even though it is still superconducting.

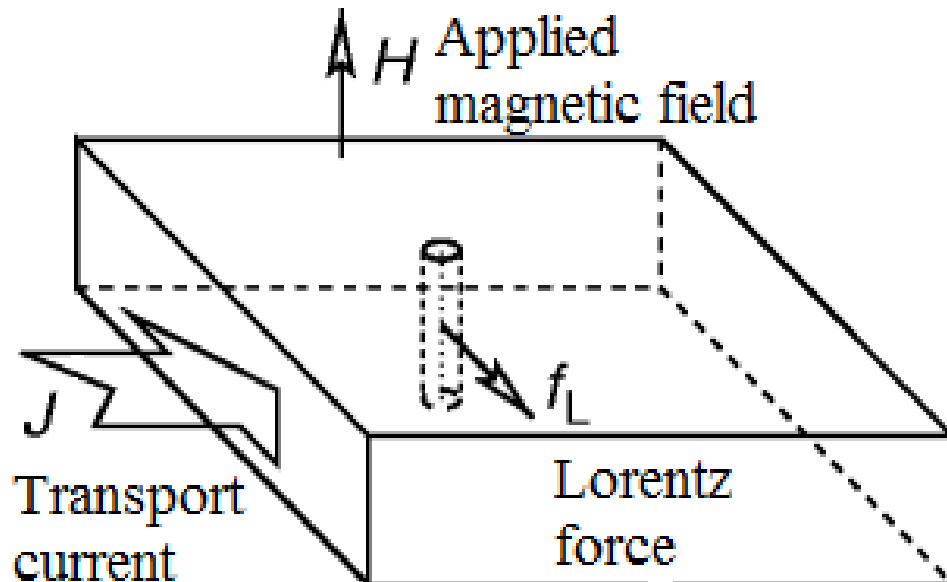


Fig. 1-15 Schematic of vortices moving under a Lorentz force.

The free movement of vortices caused by the Lorentz force can only happen in an ideal sample. In actual superconducting material containing non-superconducting defects, vortices (with their original normal cores) will be pinned onto these non-superconducting defects to minimize the total energy.

Although the formation of normal cores is energetically preferable due to the negative surface energy, the condensation energy still needs to be provided to convert the superconducting state to the normal state. So the non-superconducting defects in the material could act as pinning centers to save the condensation energy and decrease the energy spent on the flux line penetration.

Pinning forces at those defects could prevent the movement of vortices, reducing the energy losses due to the transport currents. The critical current density of superconductors could be associated with the pinning force as follows:

$$F_p = J_c \times B, \quad (1-2)$$

where F_p is the pinning force per unit volume, J_c is the critical current density and B is the flux density of the applied magnetic field perpendicular to the current.

Natural pinning centers such as dislocations, grain boundaries, stacking faults and oxygen vacancies are present in superconducting films. Artificial pinning centers with controlled shape and size have also been developed for enhancing the critical current of superconducting films in applied magnetic fields [32]. Three kinds of artificial pinning centers: linear, planar and particle defects are shown in Figure 1-16.

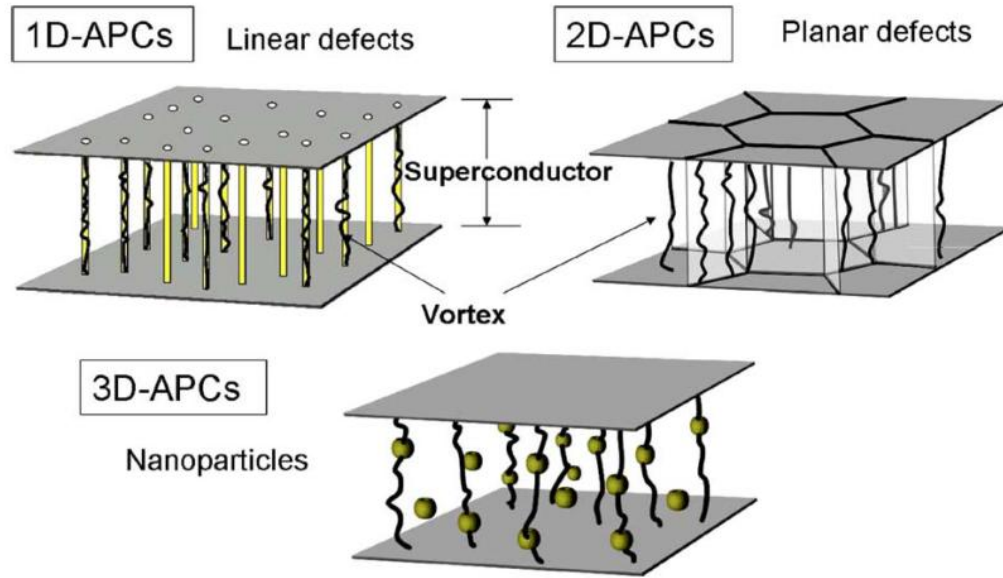


Fig. 1-16 Schematic diagram of three kinds of artificial pinning centers: linear, planar and particle defects [33].

In Figure 1-16, artificial pinning centers can be classified by structure dimensionality. The one-dimensional artificial pinning centers (1D-APCs) mainly include dislocations and columnar defects, grain boundaries and surfaces of precipitates are typical two-dimensional artificial pinning centers (2D-APCs) and the three-dimensional artificial pinning centers (3D-APCs) are dotlike defects such as fine impurity grains and nanoparticles [34].

Among these APCs, BaZrO_3 (BZO) nanocolumn defects are the most promising of the artificial pinning centers to enhance critical currents in the applied magnetic fields. In 2004, self-assembled BZO nanorods along the c-axis with diameters of 5–10 nm were realized in YBCO films by the PLD method [35]. YBCO

films with BZO nanorods were deposited from the source target of a ceramic BZO/YBCO mixture.

The critical current in the orientation of the field parallel to the c-axis ($B\parallel c$) was enhanced about two times in YBCO films with BaZrO_3 nanorods compared to the pure YBCO films. The critical currents over a wide angular orientation of magnetic field were also improved by the improved critical current at $B\parallel c$.

In the PLD method, the density of BZO nanorods could be controlled easily. Changing the BZO content of the ceramic source target will cause the variation of the BZO density in the YBCO films.

Since the MOCVD process uses a liquid precursor, the addition of Zr elements in the liquid precursor can lead to the formation of other compounds instead of the BZO under inappropriate conditions. The MOCVD condition for the growth of BZO nanorods in YBCO films was found by Selvamanickam and Chen [36], [37]. It has been found that the BZO nanorods in YBCO films processed by MOCVD still grow along the c-axis (the [001] direction) with diameters of around 5 nm and splayed over an angular range, as shown in Figure 1-17. RE_2O_3 nanoparticles are also observed as precipitate arrays along the ab planes.

In the MOCVD process, the content and distribution of BZO nanorods are mainly controlled by Zr element content (Zr doping level) in the liquid precursor.

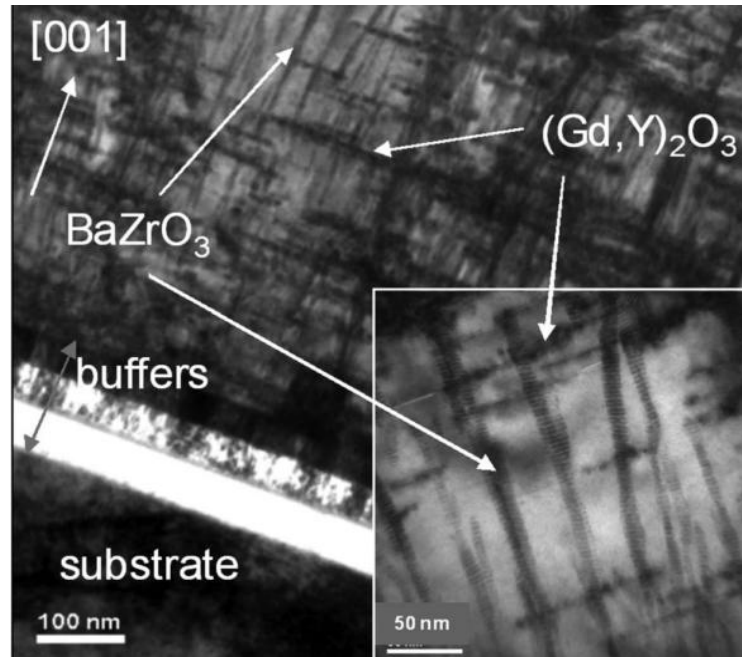


Fig. 1-17 BZO nanorods in Zr-doped GdYBCO films processed by MOCVD [37].

Although the pinning effect of BZO nanorods could enhance the critical currents in the applied magnetic field, excessive BZO nanorods which are not superconducting reduce the superconducting volume. It has been shown that Zr addition beyond 10% could lower the crystal quality and critical currents of the superconducting films [38]. In the MOCVD process, the optimization of Zr doping levels to maximize the in-field properties under different magnetic fields and temperature conditions is important and essential for applying GdYBCO superconducting films in applications.

1.4.4 In-field performance of REBCO superconducting film processed by MOCVD

The angular dependences of $(\text{Gd,Y})\text{Ba}_2\text{Cu}_3\text{O}_x$ films with different Zr doping levels processed by MOCVD are shown in Figure 1-18. The angular dependence

curve of Zr-doped (Gd, Y)BCO films includes two peaks: one peak at $H||ab$ (90° or 270°); the other peak at $H||c$ (0° or 180°).

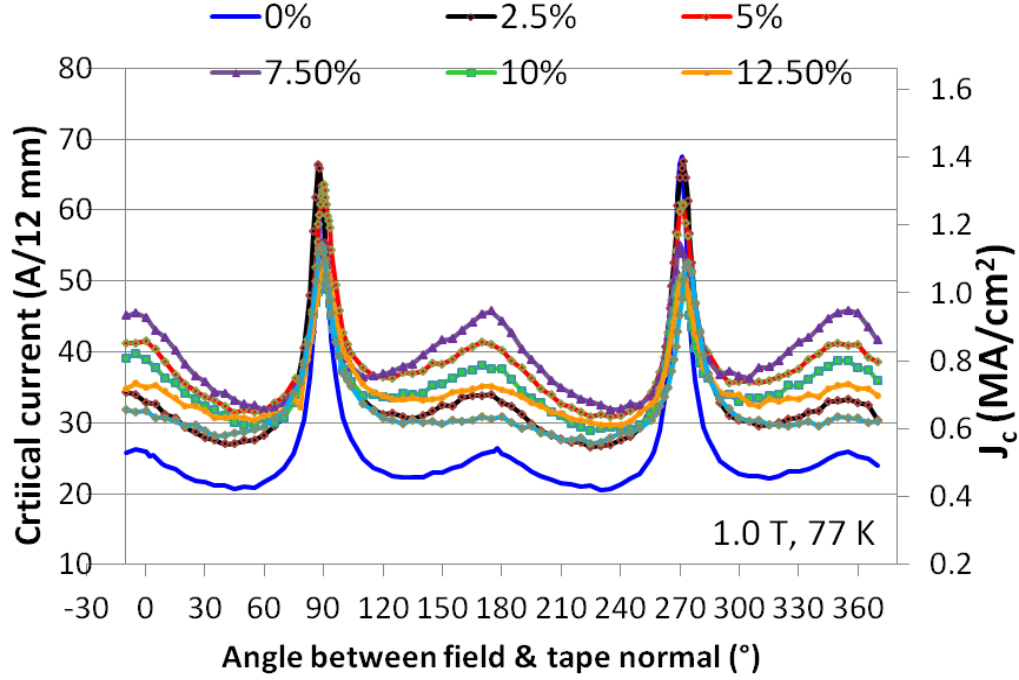


Fig. 1-18 Angular dependence of (Gd,Y)Ba₂Cu₃O_x films with Zr doping levels from 0 to 15 mol.% processed at a deposition rate of 0.16 $\mu\text{m}/\text{min}$ by MOCVD [36].

The critical current at $H||ab$ is controlled by the intrinsic pinning effects of the Cu–O layers, the ab-plane stacking faults [39] and RE₂O₃ precipitate arrays. In the lattice of YBCO, CuO₂ layers are strongly superconductive regions, separated by weakly superconductive regions. The vortices will be pinned by weakly superconductive regions between the CuO₂ planes [40]. The critical current at $H||c$ is mainly affected by the pinning effects of BZO nanorods, dislocations and grain boundaries along the c-axis.

Compared with GdYBCO films without Zr addition, the critical currents of films with Zr addition at $H \parallel ab$ (90 degrees between the field orientation and c-axis) at 77K 1T almost keep constant, while the critical currents at $H \parallel c$ are improved significantly by the enhanced pinning effect in this orientation. It shows that Zr doping could result in an effective pinning effect at $H \parallel c$ and verifies the impact of c-axis aligned BZO nano-defects. It is also seen in Figure 1-18 that 7.5% Zr doping is the optimum Zr doping level for maximizing the in-field performances of Zr-doped samples at 77K with an applied magnetic field of 1T [36].

Since a lot of HTS applications such as wind generators, marine and industrial motors need to be operated at temperatures of 20–50K with applied magnetic fields of a few Tesla, the Zr doping optimization for 77K 1T is not enough. It is necessary to fully investigate the in-field performances of Zr-doped REBCO thin films at temperatures of 20–50 K in applied magnetic fields.

The angular dependence properties of GdYBCO films with 7.5% Zr doping and 15% Zr doping at 20, 30, 40, 50K in a 3T applied magnetic field have been compared in the previous paper of our group [41], as shown in Figure 1-19. As mentioned in [41], the zero field critical currents at 77K were 382 A/12 mm for the 7.5% Zr-doped tapes and 225 A/12 mm for the 15% Zr-doped tapes.

It is found that at 77K 1T the critical current of 7.5% Zr doping at $H \parallel c$ is superior to that of the 15% Zr doping level. As the temperature decreases, the difference between the 7.5% and 15% Zr doped samples becomes smaller and smaller.

At 40 K and below, the film with the 15% Zr doping level shows a higher critical current than the 7.5% Zr-doped film. The normalized critical currents of 7.5% Zr doping and 15% Zr doping, which are the ratio of the critical current values to the 77 K zero-field critical currents, are also shown on the right side of Figure 17. At temperatures of 50 K and below, the normalized critical current of 15% Zr doping is significantly higher over the entire range of magnetic field orientations.

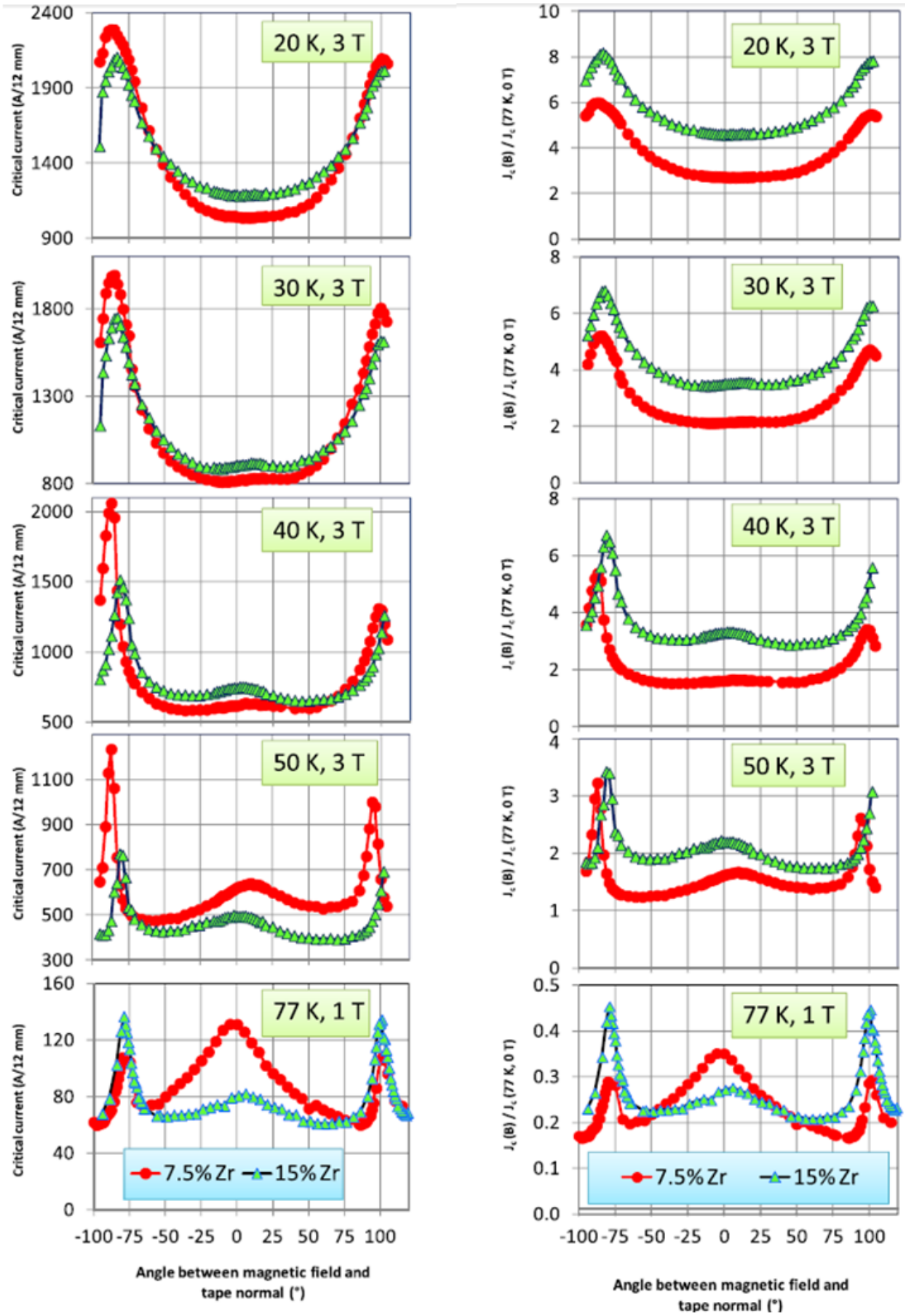


Fig. 1-19 Angular dependence of critical current and normalized critical current of GdYBCO films with 7.5% and 15% Zr doping at 20, 30, 40, 50 K with a magnetic field of 3 T and a magnetic field of 1 T at 77 K [41].

Figure 1-20 shows that the pinning force of the GdYBCO film with 15% Zr addition is significantly higher than that of the 7.5% Zr doped film at low temperatures (20K, 30K and 40 K).

The pinning defects caused by a high Zr doping level could result in a greater pinning effect at low temperatures. It is possible to achieve better in-field performance at low temperatures in REBCO samples with a Zr doping level above 15%. The in-field performance of different Zr doping levels from 0% to 30% in a wide range of temperatures and magnetic fields is investigated systematically in this work, and will be discussed in Chapter 3.

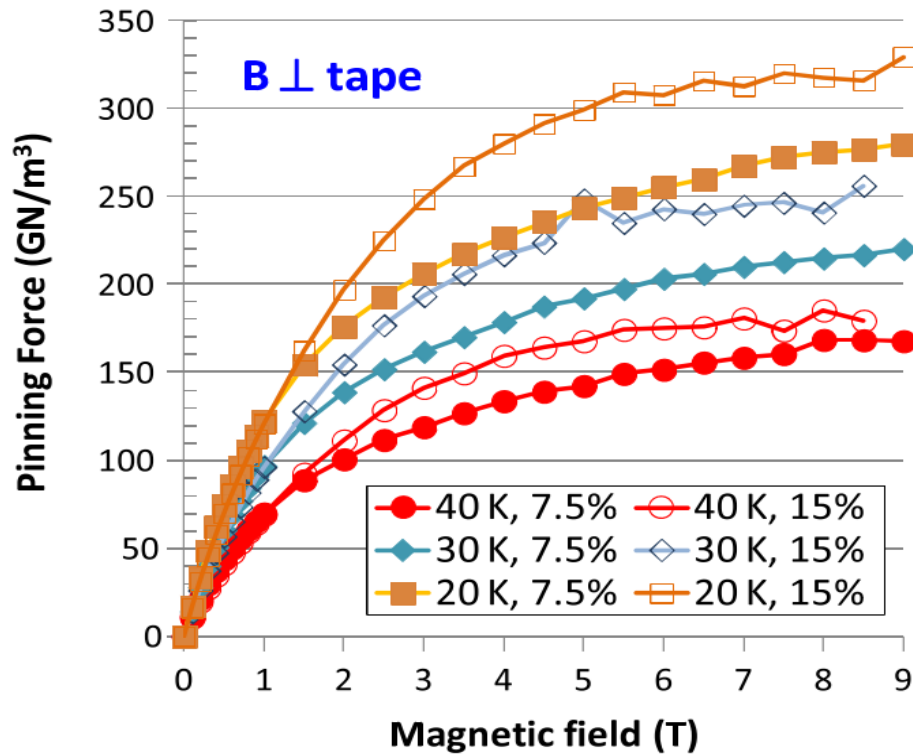


Fig. 1-20 Pinning forces of REBCO films with a 7.5% and 15% Zr addition at 20, 30 and 40 K in magnetic fields from 0 T to 9 T at $H||c$.

High Zr doping levels could cause low zero-field critical currents at 77K, which is the main reason to limit the improvement of in-field performances. Therefore if zero-field critical currents of high Zr-doped GdYBCO films can be improved as to the level of low Zr-doped films, the in-field critical currents at high Zr doping levels should be much higher compared with that at low Zr doped films at low temperatures. Therefore a modification of the MOCVD process is needed to improve the film quality of REBCO thin films at high Zr doping levels.

In this work, enhancement of critical currents of high Zr-doped GdYBCO thin films is targeted by optimization of the deposition process. The electromagnetic properties, structure and composition of Zr-doped GdYBCO are systematically investigated.

Chapter 2 Methodology

The MOCVD process used for the fabrication of REBCO thin films, post REBCO silver sputtering, oxygenation heat treatment, critical current measurement methods and microstructure measurement methods will be introduced in this Chapter.

2.1 MOCVD process for GdYBCO thin film fabrication

2.1.1 Introduction of MOCVD deposition system

A schematic diagram of a reel to reel MOCVD system is shown in Figure 2-1. A liquid precursor containing Zr, Gd, Y, Ba and Cu was delivered by a liquid pump from precursor bottles to an evaporator. Two liquid delivery lines have been designed for avoiding air contaminations during the switching of the precursor bottles. The delivery rate was kept constant at 0.25 ml/min. The evaporator is used for vaporizing the liquid precursor into gas phases at a temperature of around 270 °C. Argon is flowed into the evaporator to carry the precursor vapor into the reactor chamber.

Since oxygen could react with the precursor vapor, it is mixed with the precursor vapor at the position close to the chamber and showerhead, reducing the undesired reaction time as much as possible. The mixture of precursor vapor and oxygen is deposited on the buffer tape through a showerhead. The flow rates of argon and oxygen are controlled by mass flow controllers accurately and the chamber pressure is kept constant at 2.3 Torr, controlled by a throttle valve. The whole precursor vapor delivery line including the showerhead is heated by heating tapes to

maintain the temperature around 270 °C, the same as the temperature of the evaporator.

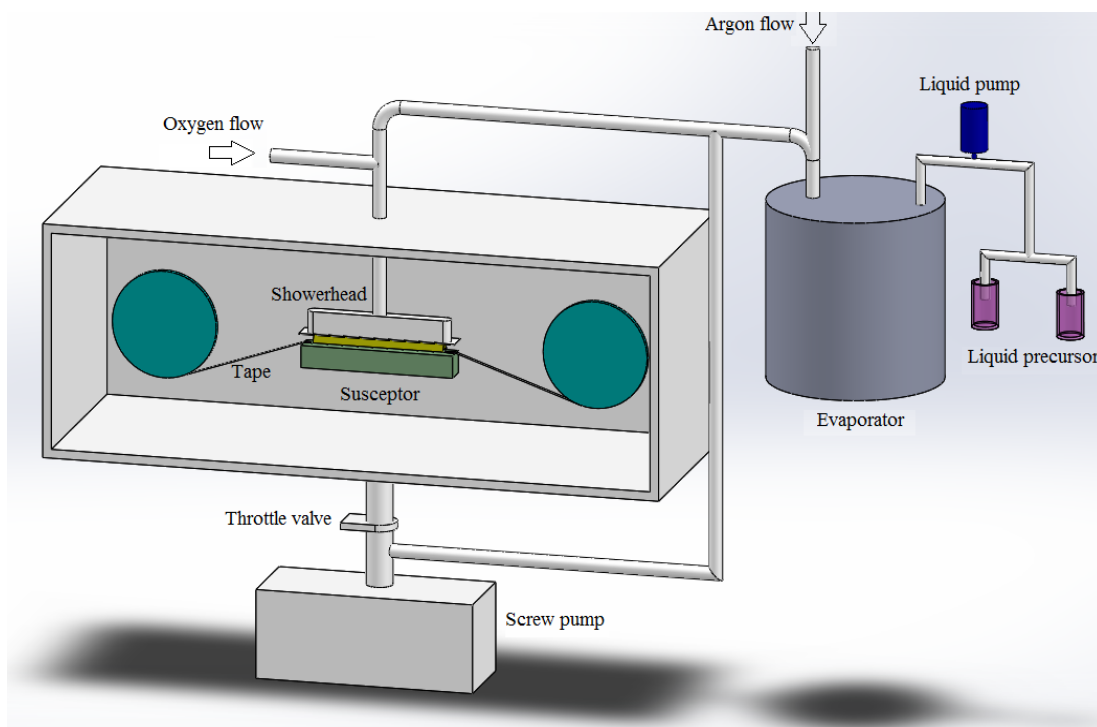


Fig. 2-1 Schematic diagram of reel to reel MOCVD system.

The buffer tapes were provided by SuperPower Inc., and consisted of an architecture of Hastelloy substrate / Al_2O_3 / Y_2O_3 / IBAD-MgO / MgO / LaMnO_3 layers, as shown in Figure 10. Using a reel-to-reel tape moving system, the buffer tapes were passed over the surface of a hot susceptor with a moving speed of 2.1 cm/min. A lamp bank array below the susceptor is the main heating source.

2.1.2 Precursor used in MOCVD process

The liquid precursors in the MOCVD process is a solution of organometallic tetramethyl heptanedionate (2, 2, 6, 6-tetramethyl-3, 5-heptanedionate) compounds of Zr, Gd, Y, Ba and Cu mixed in tetrahydrofuran solvent, as shown in Table 2-1. The

molarity of the liquid precursor was 0.05 mol/L. The molar ratio of Gd: Y: Ba: Cu in the liquid precursor is 0.6: 0.6: 2: 2.3, which is the standard precursor recipe for GdYBCO thin films processed by the MOCVD method. x% Zr doping level or x% Zr addition stands for that in the precursor solution. The molar ratio of Zr: Gd: Y: Ba: Cu is x%: 0.6: 0.6: 2: 2.3. For example, 15% Zr doping refers to the molar ratio of Zr: Gd: Y: Ba: Cu as 0.15: 0.6: 0.6: 2: 2.3.

Table 2-1 Chemistry and molar weight of elements contained in the precursor

Chemistry Formation	Molar weight
Gd(thd) ₃	707.0521 g/mol
Y(thd) ₃	639.7079 g/mol
Ba(thd) ₂ (phen) ₂	864.2724 g/mol
Cu(thd) ₃	430.0807 g/mol
Zr(thd) ₃	824.2934 g/mol

The total molar amount of organometallic tetramethyl heptanedionate compounds in the precursor was calculated as

$$n_{total} = c \times \frac{l}{v} \times q, \quad (2-1)$$

where c is the molarity of the liquid precursor, l stands for the total tape length, v is the tape moving speed and q refers to the delivery rate of the liquid precursor.

The individual compound mass could be calculated by the product of the compound molar weight and the individual molar amount.

2.1.3 Post treatments

The quality of the REBCO superconducting layer could be degraded rapidly in the moist environment. After the MOCVD deposition, a 1 μ m thick silver layer is sputtered on the film surface to protect the superconducting layer and provide good solderability for soldered current and voltage leads for electrical measurements.

The as-deposited REBCO films are actually oxygen deficient and are not superconducting. Therefore, an oxygen annealing process is necessary to fully oxygenate REBCO films. The annealing process, oxygen pressure, time span and temperature range have already been optimized for high critical current YBCO films.

The silver-sputtered REBCO thin films were placed in a horizontal tube furnace with oxygen flow. As shown in Figure 2-2, the ramp-up and ramp-down rates both were 180 $^{\circ}$ C/h and after ramping up the furnace, the temperature was maintained at 400 $^{\circ}$ C for half an hour. After cooling down, the samples were taken out for the zero-field critical current and in-field properties measurements.

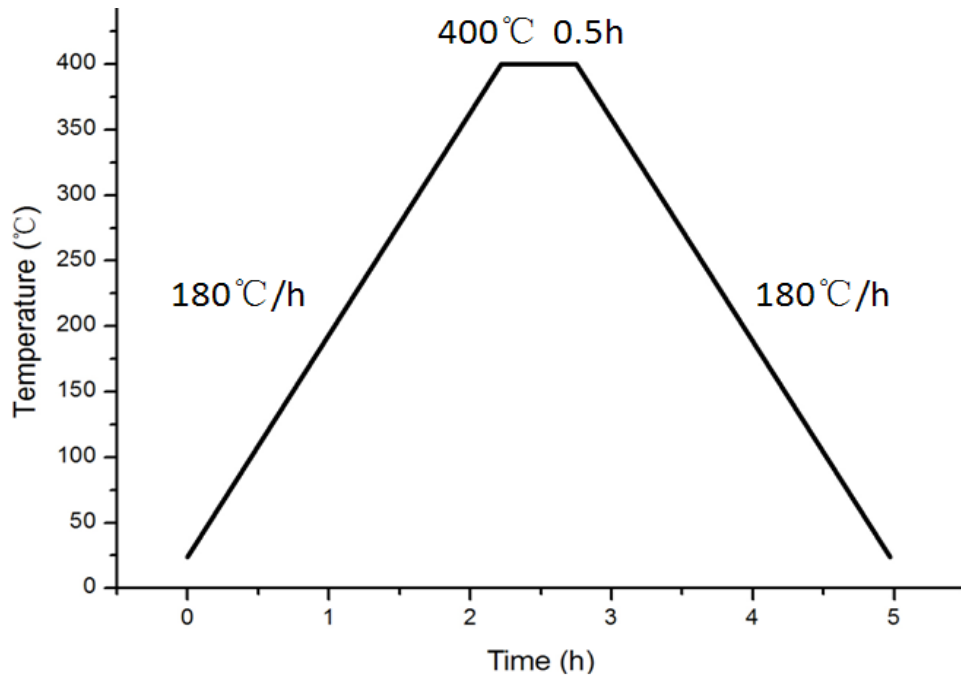


Fig. 2-2 Oxygen annealing procedures of MOCVD processed REBCO thin films.

2.2 Critical current measurements

A schematic diagram of critical current measurement is shown in Figure 2-3. After the oxygen annealing process, the REBCO superconducting tapes with sputtered-silver layers are attached with silver tapes by indium solder. Then the silver tapes are connected with copper current leads. Since sometimes the sputtered-silver layer can be damaged by the tips of a soldering pencil at a temperature above 200 °C, an indium solder with a melting point of 156°C is used.

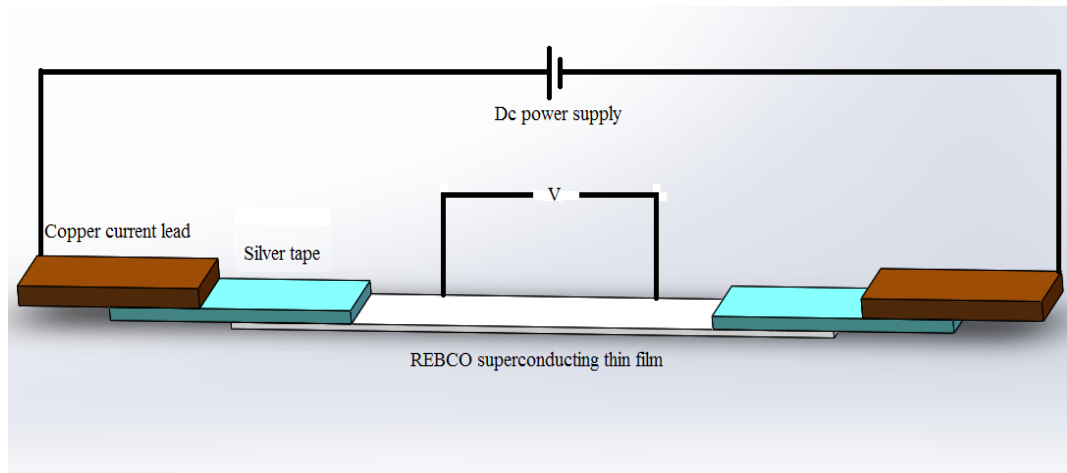


Fig. 2-3 Schematic diagram of critical current measurement.

A four-probe method is used in critical current measurements. The transport current from a DC current power supply is passed through the REBCO superconducting tape. Two voltage detecting probes are connected on the surface of the REBCO superconducting tape. During the measurement, the current generated by the DC current power supply is increased at a constant ramp-up rate. When the current is lower than the critical current, no voltage is detected because of zero resistance under the superconductive state. When the current reaches the level of the critical current, the sample will transfer into the normal state with a resistivity, leading to a voltage drop immediately.

Although the REBCO superconducting tapes could carry transport currents up to around 1000A, the soldered joints in critical current measurements will cause too much heat and damage the samples if the transport current is above 500A. For constraining the carrying transport current to a safe value, a chemical etching method is used for pattern the width of superconducting tapes. As shown in Figure 2-4, a

bridge with the width of 1~2mm is achieved by the chemical etching method. At first, the surface of a full-width sample is covered by Kapton® tapes with a shape like the white region shown in Figure 2-4. The Kapton tape can protect the sample surface from chemical etching, so the region without Kapton tape (purple region in Figure 2-4) will be removed by chemical solutions. Then, the silver layer of the region not covered by Kapton tape is etched by the silver etching solution (the mixture of 50% ammonium hydroxide and 50% hydrogen peroxide). Finally, the REBCO superconducting layer is removed by 10 vol% nitric acid.

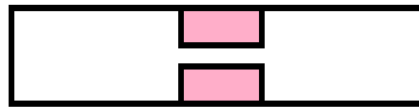


Fig. 2-4 Schematic diagram of REBCO tape with bridging.

Zero-field critical current at 77K is measured in the liquid nitrogen without an applied magnetic field. Zero-field critical current at 77K is helpful to characterize the film quality.

The in-field critical current is measured at different temperatures and magnetic fields. The REBCO tape is mounted on a sample holder which is turned by a rotator for measuring critical currents at different angles between magnetic field and tape normal direction, maintaining the field always perpendicular to the current flow direction. In this work, a custom-designed cryogen-free 9 Tesla electromagnetic characterization system by Cryogenic, Ltd. was used for in-field electromagnetic property measurement, as shown in Figure 2-5. The system is made up of a motorized

stage with all wiring, an aluminum alloy vacuum cryostat, two cryocoolers, a gas bag and a control system. The vacuum cryostat contains the superconducting magnet, cryogenic circulation and heaters. The sample is installed on the sample platform located at the end of the motorized stage, which can be rotated to the required angles between tape normal orientation and magnetic field orientation accurately.

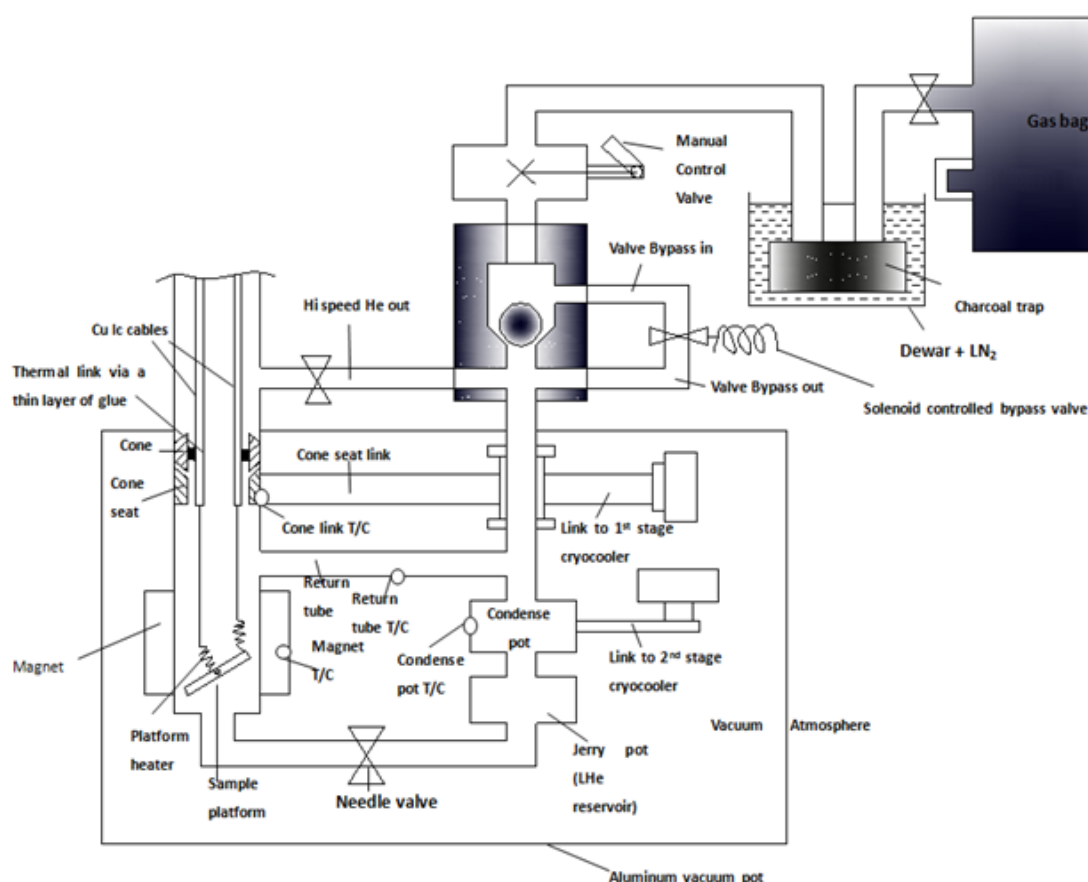


Fig. 2-5 Schematic diagram of cryogen-free electromagnetic characterization system.

2.3 Sample microstructure characterization

A scanning electron microscope (SEM) is used for analyzing surface morphology of REBCO thin films. Since REBCO thin films have a strong preferential texture, an X-ray diffraction (XRD) with a Bruker General Area Detector Diffraction System (GADDS) is used to collect two-dimensional x-ray diffraction information for

phase identification and quantitative analysis. Different phases can be identified by the diffraction angle. After integration over a selected area, the peak intensities are used for quantitative analysis.

Cross-sectional and plan-view microstructures of REBCO thin films were investigated by transmission electron microscopy (TEM). Cross sectional samples were prepared by focused ion beam (FIB), cut into 5 μ m long sample bars and then polished to be electron transparent. Plan-view samples are obtained by Ar ion milling the tapes from the Hastelloy side until the film becomes electron transparent [42].

2.4 Elemental analysis of REBCO thin film

The microstructure variation of REBCO thin films is mainly related to the variation of second phases, which could also lead to the variation of element contents in the films. In this work, Agilent 7700 Series inductively coupled plasma-mass spectrometry (ICP-MS) was employed for elemental analysis of REBCO thin films. Inductively coupled plasma mass spectrometry can detect the concentration of materials with an atomic mass from 7 to 250 accurately. It can scan multiple elements simultaneously to achieve a rapid sample processing rate.

As shown in Figure 2-6, for ICP measurement, a 0.5cm long REBCO sample is dissolved into 20ml 2 vol.% nitric acid. The solution is pumped into a simple nebulizer to form an aerosol. Larger aerosol droplets are removed from the gas stream by a spray chamber, and the remaining smaller droplets are passed into an argon plasma channel. In high temperature plasma (around 7,500K), the aerosol droplets are

rapidly dried, decomposed, vaporized and atomized, then ionized by the removal of one electron from each atom. A series of electrostatic lenses keep the ions focused in a compact "ion beam," which passes through the vacuum system to the mass spectrometer (MS) and detector. In the mass spectrometer, a combination of DC (direct current) and AC (alternating current) electrical fields are applied to separate ions based on their mass to a charge ratio (m/z).

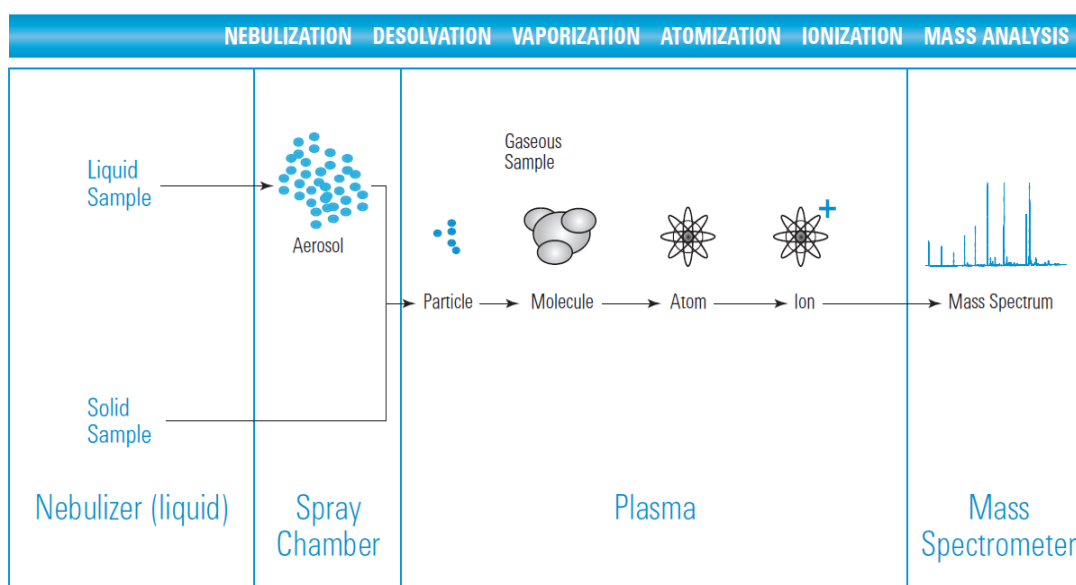


Fig. 2-6 Schematic diagram of processes in ICP-MS from sample preparation to mass analysis [43].

After obtaining the molar concentrations of Zr, Gd, Y, Ba and Cu, the relative content of the individual element is calculated by the ratio of single element's molar concentration to the molar concentration summation of the whole five elements.

Chapter 3 Result and Discussion

The electromagnetic property of GdYBCO thin film with low Zr doping levels from 0% to 15% fabricated by MOCVD process has been studied systematically in our previous work. It showed that at 77K1T, 7.5% addition was the optimal Zr level for critical current at magnetic field parallel to c axis [36]. Since high temperature superconductors (HTS) is a potential material to apply in wind generators, industrial motors, with operating conditions of temperatures from 20K to 50 K and magnetic fields from 0T to 5 T, it is not enough to optimize the infield performance of Zr doped GdYBCO thin films just at 77K. At low temperatures (20~40K), GdYBCO tapes with 15% Zr addition performed significantly superior to 7.5% Zr doped tapes from 1 to 9 T [41]. It indicated that at lower temperature, higher Zr doping level has the promising potential for better infield performance.

However, an important issue is that increasing Zr doping level from 7.5% to 30 % caused significant degradation of zero field critical current and critical current in field orientation parallel to c-axis. In this work, using a modified MOCVD process, the critical current degradation with increasing Zr content was reduced. The influence of Zr doping levels from 7.5 to 30 mol.% on the electromagnetic properties of GdYBCO films processed by the improved MOCVD process was investigated at low temperatures and high magnetic fields over a wide angular range of field orientations.

3.1 Susceptor temperature optimization of MOCVD process for high levels of Zr-doped REBCO film

Susceptor temperature is the most important temperature variable for the growth of Zr-doped GdYBCO film in the MOCVD process, which needs to be controlled precisely and stably. It is found that the self-field critical current of Zr-doped GdYBCO film is sensitive to susceptor temperature variation as shown in Figure 3-1.

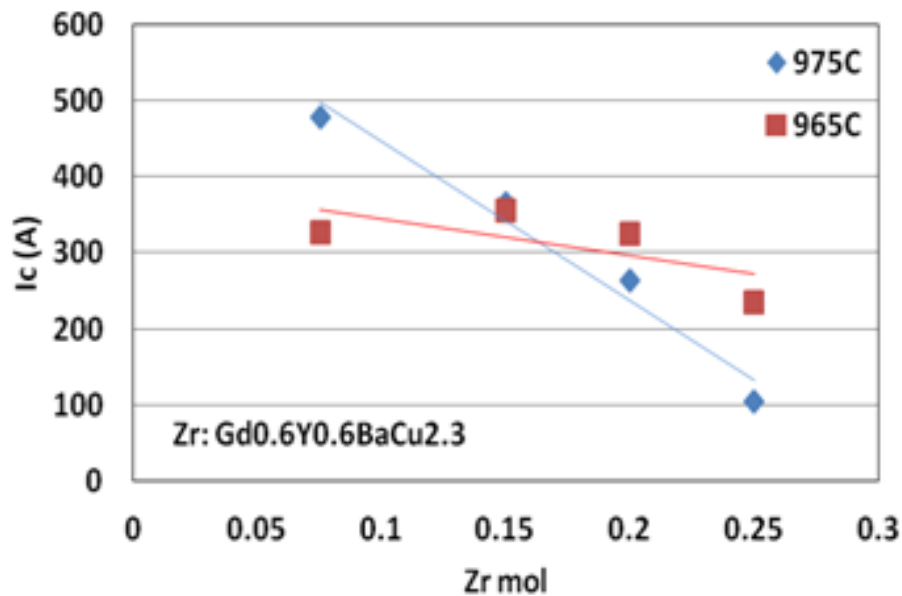


Fig. 3-1 Self field critical currents of (Gd,Y)BCO tapes with Zr doping levels from 7.5% to 25% at two susceptor temperatures — 965°C and 975°C.

At the optimized precursor mole ratio of Gd: Y: Ba: Cu (0.6: 0.6: 2: 2.3) and the same reactor pressure (2.3Torr), the relationship of Zr doping level and self field critical current were investigated. In Figure 3-1, the variation of self field critical currents of tapes with different Zr doping levels at two susceptor temperatures — 965°C and 975°C are shown. At 975°C, the critical current is found to decrease

linearly with increasing Zr doping level. It means that the optimal Zr doping levels of self field critical current at different susceptor temperatures are different.

According to the data shown in Figure 3.1, a linear dependence between susceptor temperature and optimal Zr doping level was assumed to fit with two points (0.075, 975 °C) and (0.15, 965 °C) in order to determine temperature conditions for different Zr doping levels in the experiment, which are shown in Table 3-1. The precursor molar ratio of Gd: Y: Ba: Cu was 0.6: 0.6: 2: 2.3. The thickness of GdYBCO samples was about 0.8 μm .

Table 3-1 Process Information of Zr-doped GdYBCO

Precursor Content ratio (Zr: Gd: Y: Ba: Cu)	Deposition rate ($\mu\text{m}/\text{min}$)	Susceptor Temperature (°C)
0: 0.6: 0.6: 2: 2.3	0.1	980
0.05: 0.6: 0.6: 2: 2.3	0.1	977
0.075: 0.6: 0.6: 2: 2.3	0.1	975
0.1: 0.6: 0.6: 2: 2.3	0.1	971
0.125: 0.6: 0.6: 2: 2.3	0.1	968
0.15: 0.6: 0.6: 2: 2.3	0.1	965
0.2: 0.6: 0.6: 2: 2.3	0.1	960
0.25: 0.6: 0.6: 2: 2.3	0.1	955
0.3: 0.6: 0.6: 2: 2.3	0.1	950

At a high deposition rate the growth of BZO in high Zr-doped samples could interfere with the crystallinity of GdYBCO [38]. A low molarity of 0.05 M/L was used to obtain a low deposition rate as 0.1 $\mu\text{m}/\text{min}$, which is four-fold lower than that of the standard MOCVD process. The tape speed was lowered four-fold 2.1 cm/min so that the same film thickness (~ 0.9 to 1 μm) is achieved.

The contents of Zr, Gd, Y, Ba and Cu in the superconducting film were measured by inductively coupled plasma (ICP) spectroscopy. As shown in Figure 3-2, the amount of Zr addition in the precursor resulted in a linear increase in Zr content in the superconducting film. It is also found that the content of copper in the film decreased with increasing Zr addition. In comparison with Zr and Cu, the content of Ba, Y and Gd don't change significantly. In particular, the contents of Gd and Y in the film remain almost keep the same over the entire range of Zr doping.

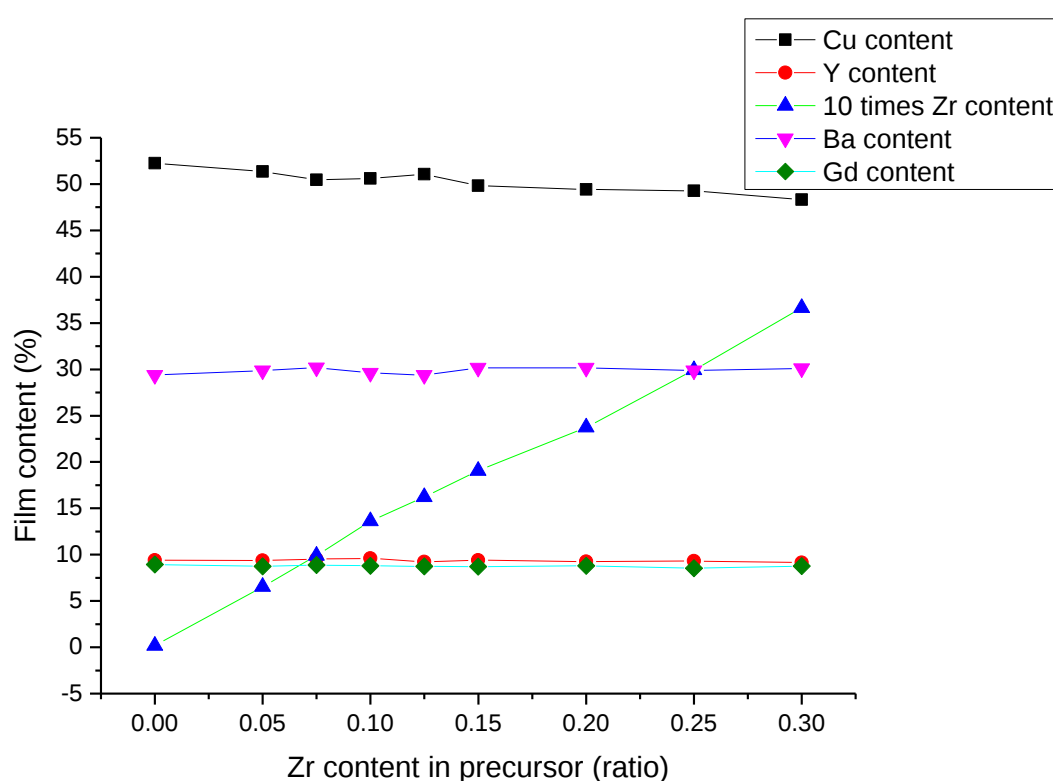


Fig. 3-2 Comparison of Zr content in the precursor and Zr content in the film.

Figure 3-3 shows the improvement in 77 K, zero field critical current of samples with high levels of Zr addition by modified MOCVD process. It can be seen that in standard process, the self field critical current drops sharply from 7.5% Zr

doping while the critical current of samples processed by modified MOCVD process varies slightly from 5% to 15% and drops from 15% to 30%. In the 25% Zr doped sample, the zero field critical current increased from 40 A to 280 A after process modification. The improved critical current gave us an opportunity to achieve better in-field critical currents at high Zr doping levels.

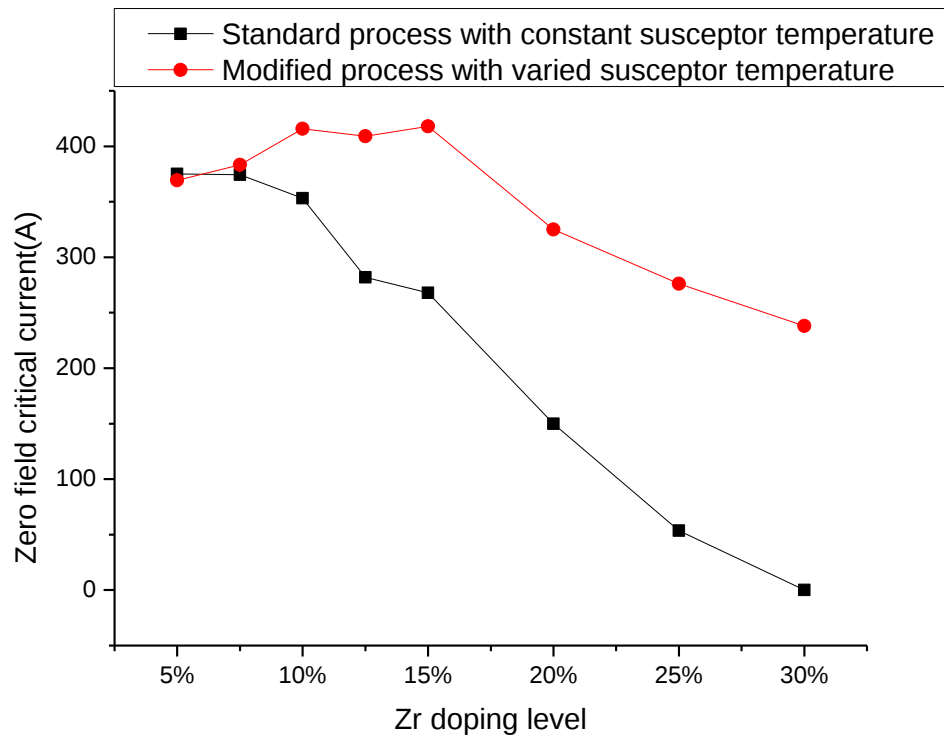


Fig. 3-3 Plot of 77 K, self field critical current vs Zr doping level in modified MOCVD process and standard MOCVD process.

3.2 In-field property of REBCO film with high Zr doping level

The in-field performances of GdYBCO samples with Zr doping level varying from 7.5 to 30 % at 77K, 65K, 50K, 40K and 1T, 3T, 5T are shown in Figure 3-4.

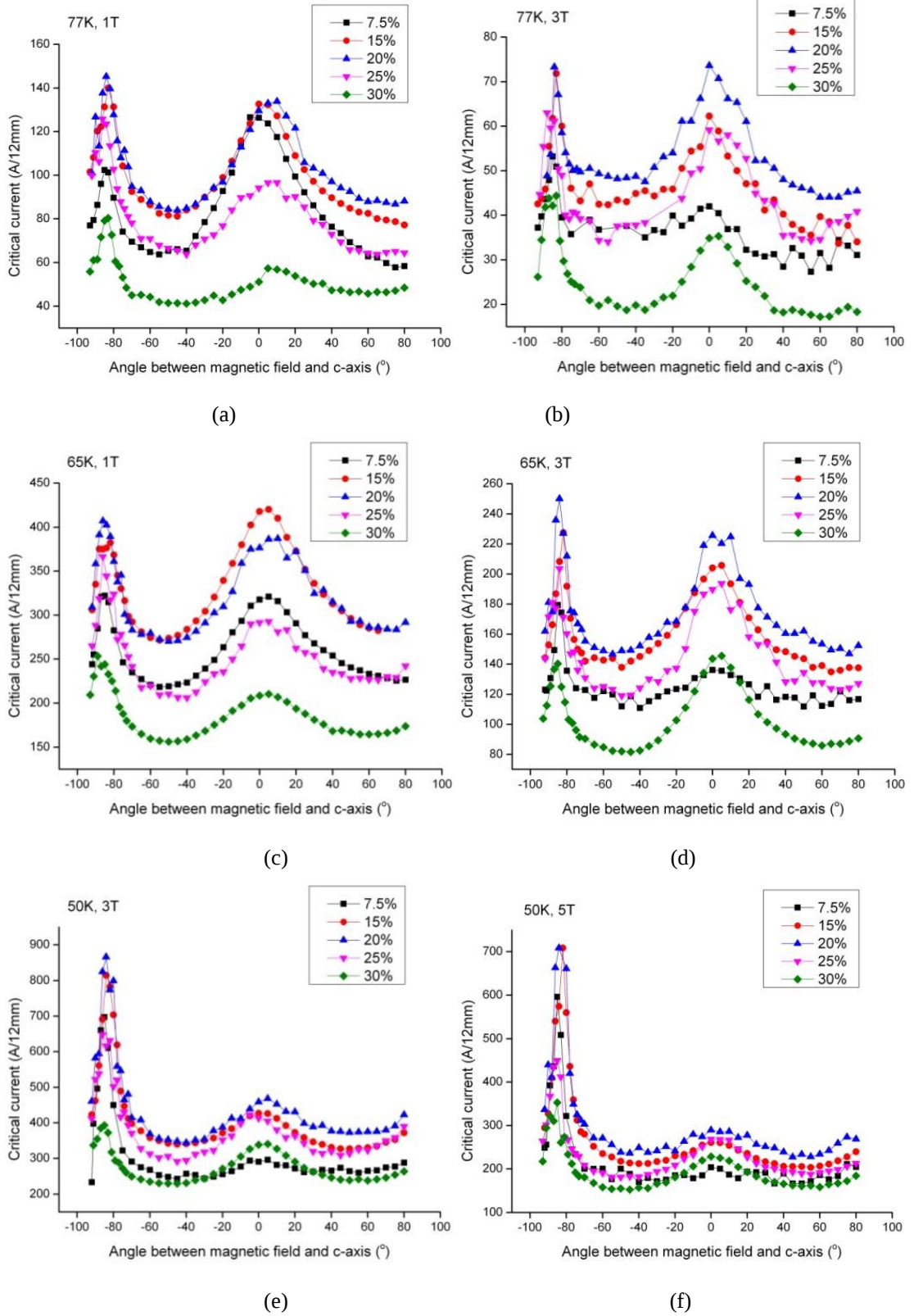


Fig. 3-4 Angular dependence of critical current of GdYBCO tapes with 7.5-30 mol.% Zr doping at (a) 77K 1T, (b) 77K 3T, (c) 65K 1T, (d) 65K 3T, (e) 50K 3T, (f) 50K 5T.

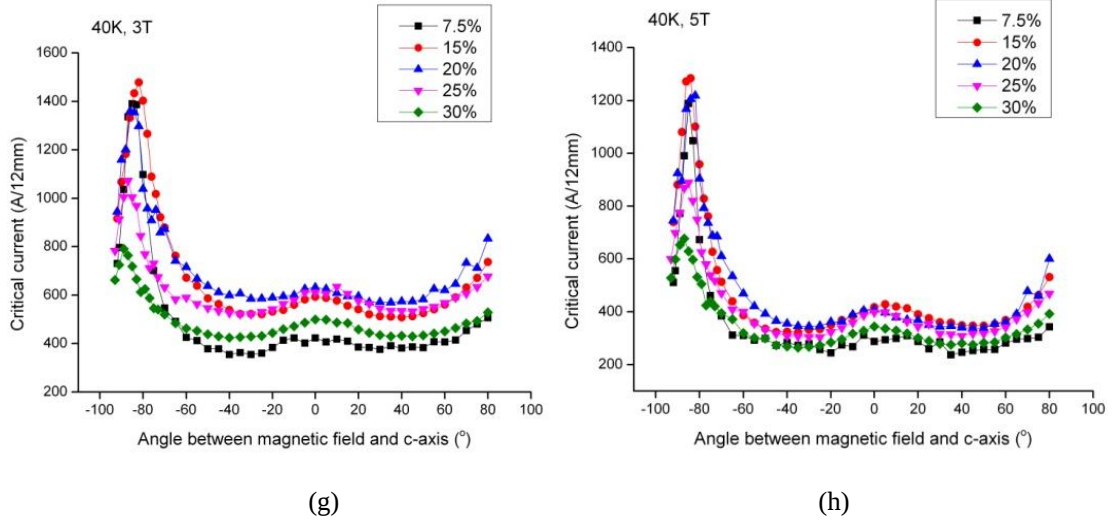


Fig. 3-4 Angular dependence of critical current of GdYBCO tapes with 7.5-30 mol.% Zr doping at (g) 40K 3T, (h) 40K 5T, (continued).

In Fig. 3-4(a), at 77K 1T, the 7.5% Zr doped sample shows the maximum critical current in the orientation of $H||c$ among samples processed by the modified MOCVD process. Samples with 15% and 20% Zr have equally good critical currents at $H||c$ as 7.5% Zr doped sample and higher critical currents at $H||ab$ compared with 7.5% Zr-doped samples, resulting in better infield performance over the entire range of field orientation. In Fig. 3-4(b), at 77 K 3T samples with 15%, 20% and even 25% Zr show higher critical currents compared with 7.5% Zr doped sample. Obviously, at 77K 3T sample with 20% Zr addition shows the highest critical current over the entire range of field orientation, although the zero field critical current of 20% Zr doped sample at 77K is only 75% of that of 7.5% Zr doped sample.

By decreasing the temperature to 65 K, as shown in Fig. 3-4(c) and (d), the performance of samples with 15% and 20% Zr doping become far superior compared with the sample with 7.5% Zr doping. In Fig. 3-4(d), at 65 K, 3 T, the critical current

peak of 7.5% Zr-doped sample around the orientation of $H||c$ becomes not significant, and exhibits the lowest critical current at $H||c$ compared with samples with higher Zr addition (15 to 30%). Considering the fact that the zero field critical current of 30% Zr at 77K is less than 50% of that of the 7.5% Zr doped sample, a higher critical current of 30% Zr doping at $H||c$ than 7.5% Zr doping provides a convincing proof for the improvement effect of in-field performance by high levels of Zr doping.

In Fig. 3-4(e) and (f), at 50 K 3T and 50K 5T, the in-field performance of 7.5% Zr-doped samples was depressed below all the other samples. The 20% Zr-doped samples still displays the highest critical current at $H||c$, and the best angular dependence characteristic over the entire range of measured field orientations. As the temperature is reduced to 40K, the angular dependence characteristics don't change obviously from those at 50K. In Fig. 3-4(h), it is seen that at 40K 5T the differences in in-field performance curves of samples with different Zr doping levels become small.

The minimum critical current of in-field performance is an important criterion, defining the upper limit of current transport capability for applying superconducting tapes in magnetic fields with random orientations. Figure 3-5 shows the relationship between Zr addition level and minimum critical current in angular dependence curves.

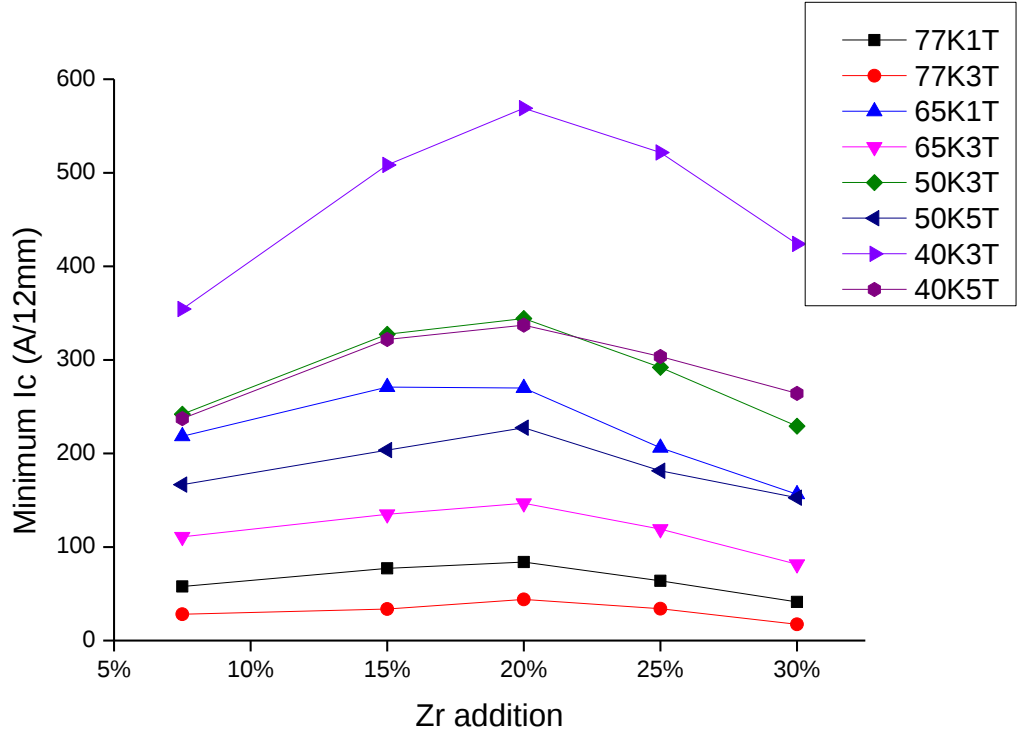


Fig. 3-5 Influence of Zr addition on minimum critical current of GdYBCO tapes at 77K, 65K, 50K, 40K and 1T, 3T, 5T.

From this figure, it is seen that the 20% Zr-doped sample displays the highest minimum critical current at all temperatures and magnetic field conditions used in these measurements. At 40K 3T, the minimum critical current of 20% Zr-doped tape is 60% higher than the minimum critical current of 7.5% Zr-doped tape. Considering that 20% Zr doped sample also has the highest critical current at $H||c$, it indicates that 20% Zr addition is the optimal addition for in-field performance of Zr-doped GdYBCO tapes over a wide range of temperature and magnetic field conditions.

In-field performance could be considered as the product of the interaction between film quality which is usually reflected in self-field critical current at 77K, and pinning center structure which impacts in-field performance. Figure 3-6 shows

the ratio of the minimum critical current in in-field performance curves to the self-field critical current at 77K.

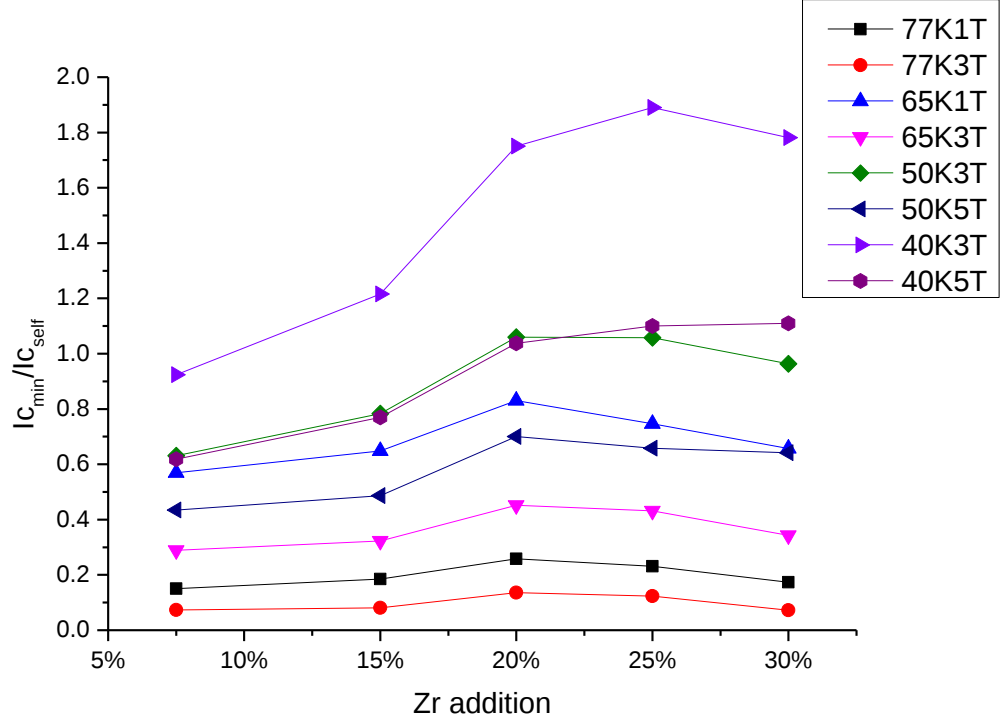


Fig. 3-6 Influence of Zr addition on the ratio of minimum critical current to 77K self-field critical current 77K, 65K, 50K, 40K and 1T, 3T, 5T.

As shown in Figure 3-6, the ratios of the minimum critical current to the self-field critical current at 77K display peak values at about 20% Zr doping from 50K to 77K. At 40K, it is found that the Zr doping level with maximum ratio shifts to 25%. It shows that there is still potential for Zr doping level above 20% to obtain better minimum critical current by adjusting and optimizing MOCVD process condition.

As reported in [36], in Zr-doped GdYBCO tapes the critical current peak value at $H||c$ is mainly determined by pinning effect of c-axis-aligned BZO nanocolumns. The ratio of critical current at $H||c$ to 77K self-field critical current, called the ‘lift

factor,' could reflect the pinning effect of c-axis aligned BZO nanorods directly. The ratios of critical current of (Gd,Y)BCO tapes with different Zr doping levels at B||c to 77K self-field critical current at 77K, 65K, 50K, 40K and 1T, 3T, 5T are shown in Figure 3-7.

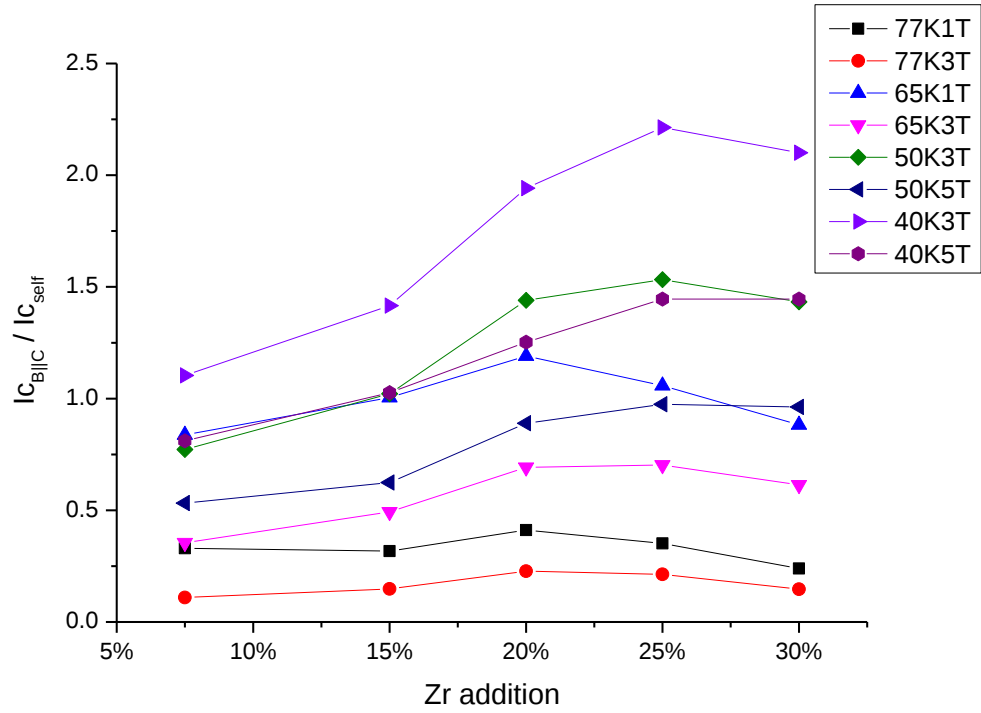


Fig. 3-7 Influence of Zr addition on the ratio of critical current of (Gd,Y)BCO tapes at B||c to 77K self-field critical current at 77K, 65K, 50K, 40K and 1T, 3T, 5T.

In Figure 3-7, at 65K and 77K, the lift factor of 20% Zr doping level shows the maximum value. As the temperature goes down to 40K and 50K, the optimal Zr doping level for the best lift factor shifts to 25% Zr doping.

From the results in Figure 3-6 and Figure 3-7, it concluded that the pinning center structure of 25% Zr doping level is preferable for improving the in-field performance at low temperature around 40K. Next, the magnetic field dependence of

critical current and pinning force at $H||c$ of Zr-doped GdYBCO was studied in this work. Pinning force is calculated by $F_p = J_c \times B$, where F_p is the pinning force, J_c is the critical current density, B is the magnetic field. Figure 3-8 shows magnetic field dependencies of critical current and pinning force at $H||c$ of GdYBCO tapes with 7.5, 20% and 30 % Zr doping measured from 0T to 5T at 77K, 65K, 50K and 40K.

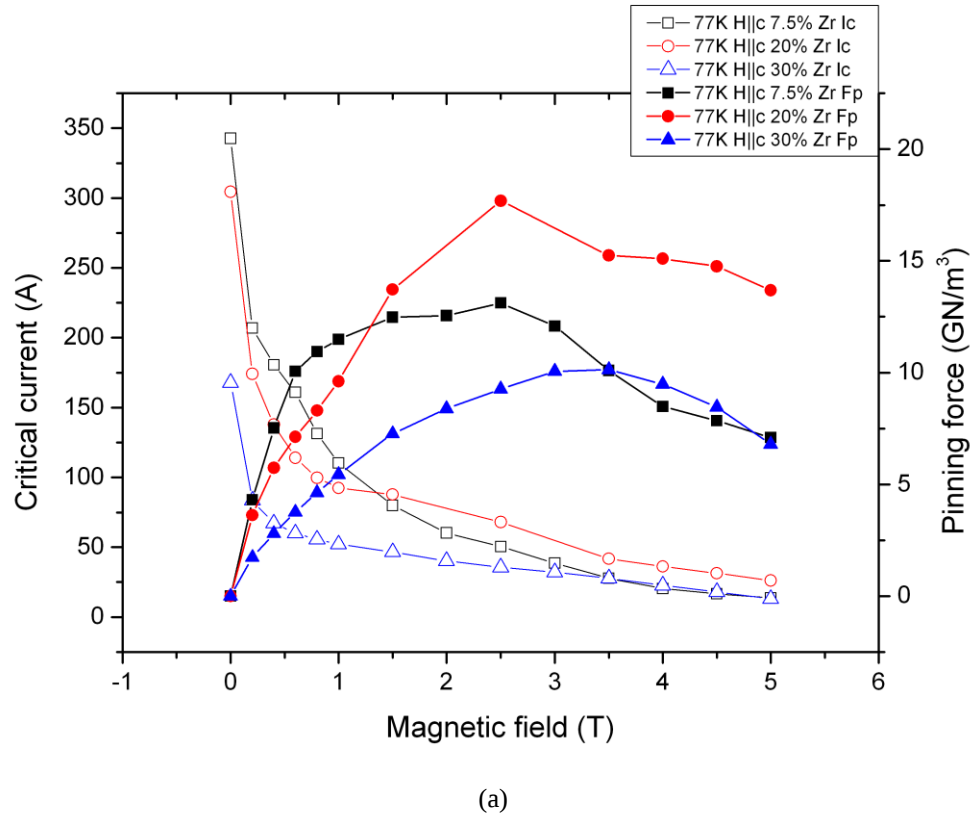


Fig. 3-8 Magnetic field dependence of critical current and pinning force at $H||c$ of GdYBCO tapes with 7.5, 20% and 30% Zr doping at (a) 77K.

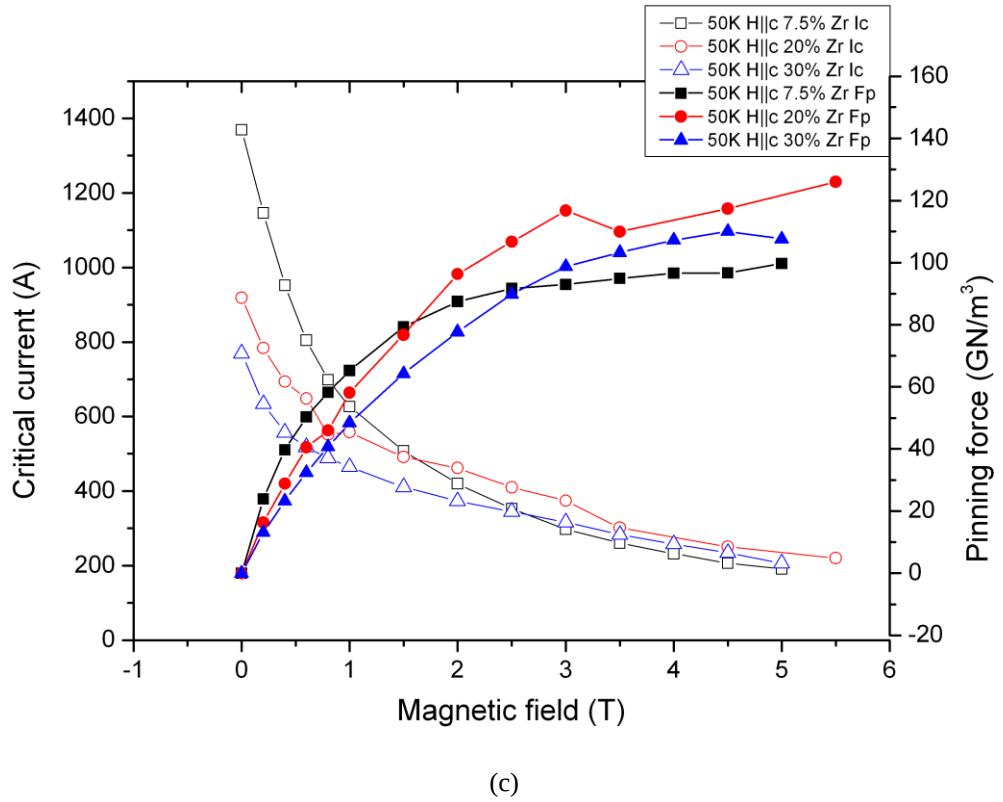
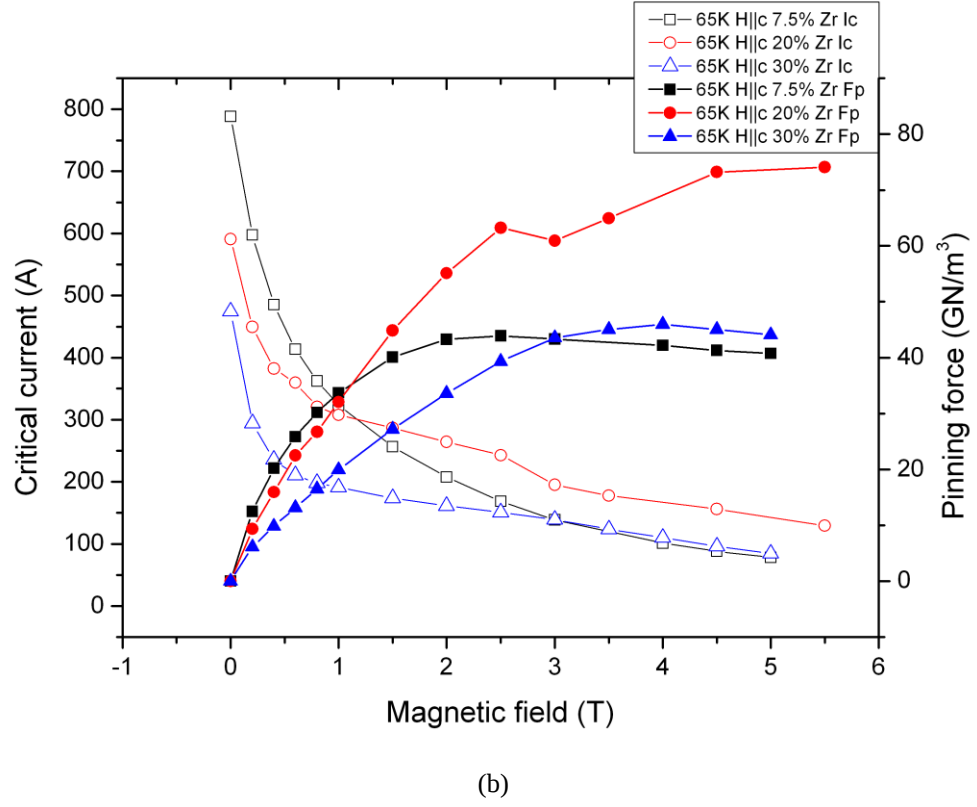


Fig. 3-8 Magnetic field dependence of critical current and pinning force at H||c of GdYBCO tapes with 7.5, 20% and 30% Zr doping at (b) 65K, (c) 50K, (continued).

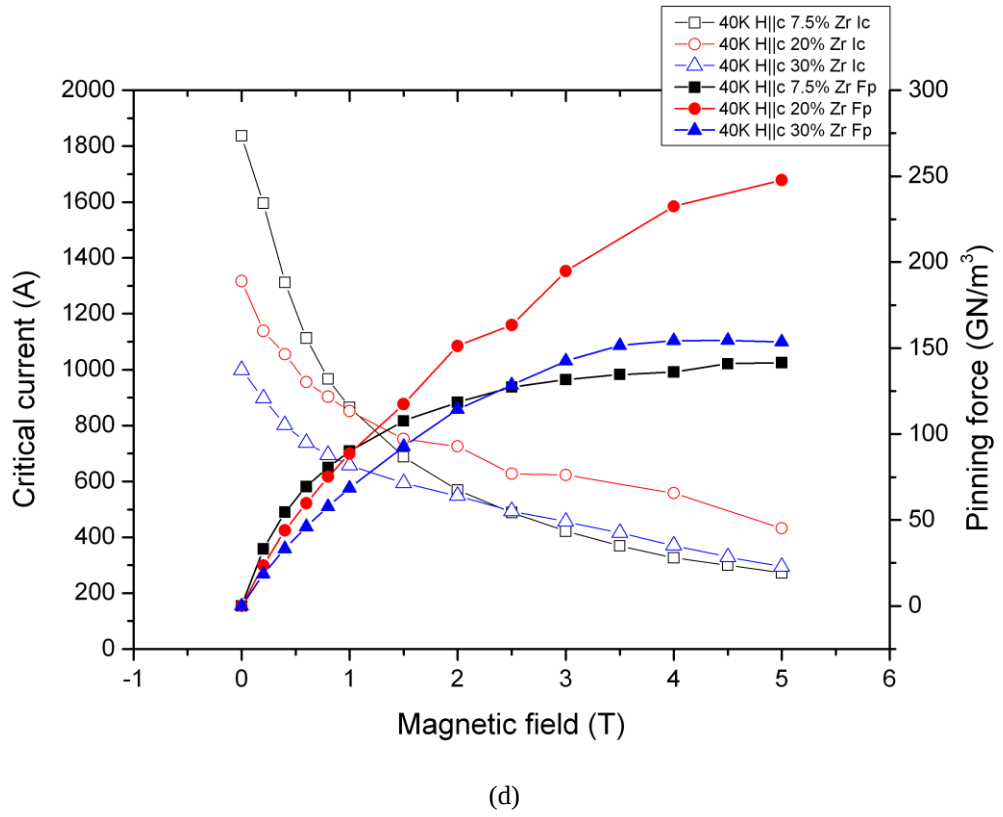


Fig. 3-8 Magnetic field dependence of critical current and pinning force at H||c of GdYBCO tapes with 7.5, 20% and 30% Zr doping at (d) 40K, (continued).

In Figure 3-8, it is found that the critical current and pinning force at H||c of 20% Zr doped samples are always superior to those of samples at 30% Zr doping level over a wide range of magnetic fields (0T~5T) and temperatures (40K~77K). From 0T to 1T, the 7.5% Zr-doped sample shows the highest critical current and pinning force at H||c. From 1T to about 2.5T, the critical current and pinning force at H||c of 7.5% Zr doping are lower than the sample with 20% Zr doping, higher than the sample with 30% Zr doping over all the temperatures. As increasing magnetic field above 3T, even the sample with 30% Zr doping displays higher critical current and pinning force at H||c compared with the sample with 7.5% Zr doping.

From Fig. 3-8, it is also seen that at high magnetic fields above 1.5T, the difference of pinning force between 20% and 7.5% or 30% enlarges with increasing magnetic field, which suggests that 20% Zr doping could lead to better pinning performance at higher magnetic field.

In this section, the angular dependence and field dependence of GdYBCO tapes with 7.5%, 15%, 20%, 25% and 30% Zr doping have been investigated over a wide range of temperature (40K~77K) and magnetic field (0T~5T). In summary, some conclusions could be obtained:

1. 20% Zr doping is the optimal Zr doping level for critical current at $H||c$ and minimum critical current over a wide range of temperature and magnetic field conditions and is especially preferable at low temperatures around 40K.
2. The influences of Zr addition on the ratio of the minimum critical current to 77K self-field critical current and on the ratio of critical current at $H||c$ to 77K self-field critical current follow the similar tendency: at temperatures above 50K, the peak values occur at 20% Zr doping level; at 40K, the best values occur to 25% Zr doping.
3. At high magnetic fields above 1.5T, 20% Zr doping shows the best pinning performance. Compared with 7.5% Zr doping, a high Zr doping level above 20% could provide higher pinning force at high magnetic fields.

3.3 Microstructural study of high levels of Zr-doped REBCO film

Structure variation of GdYBCO samples with increasing Zr content was investigated by 2-dimensional XRD, as shown in Figure 3-9.

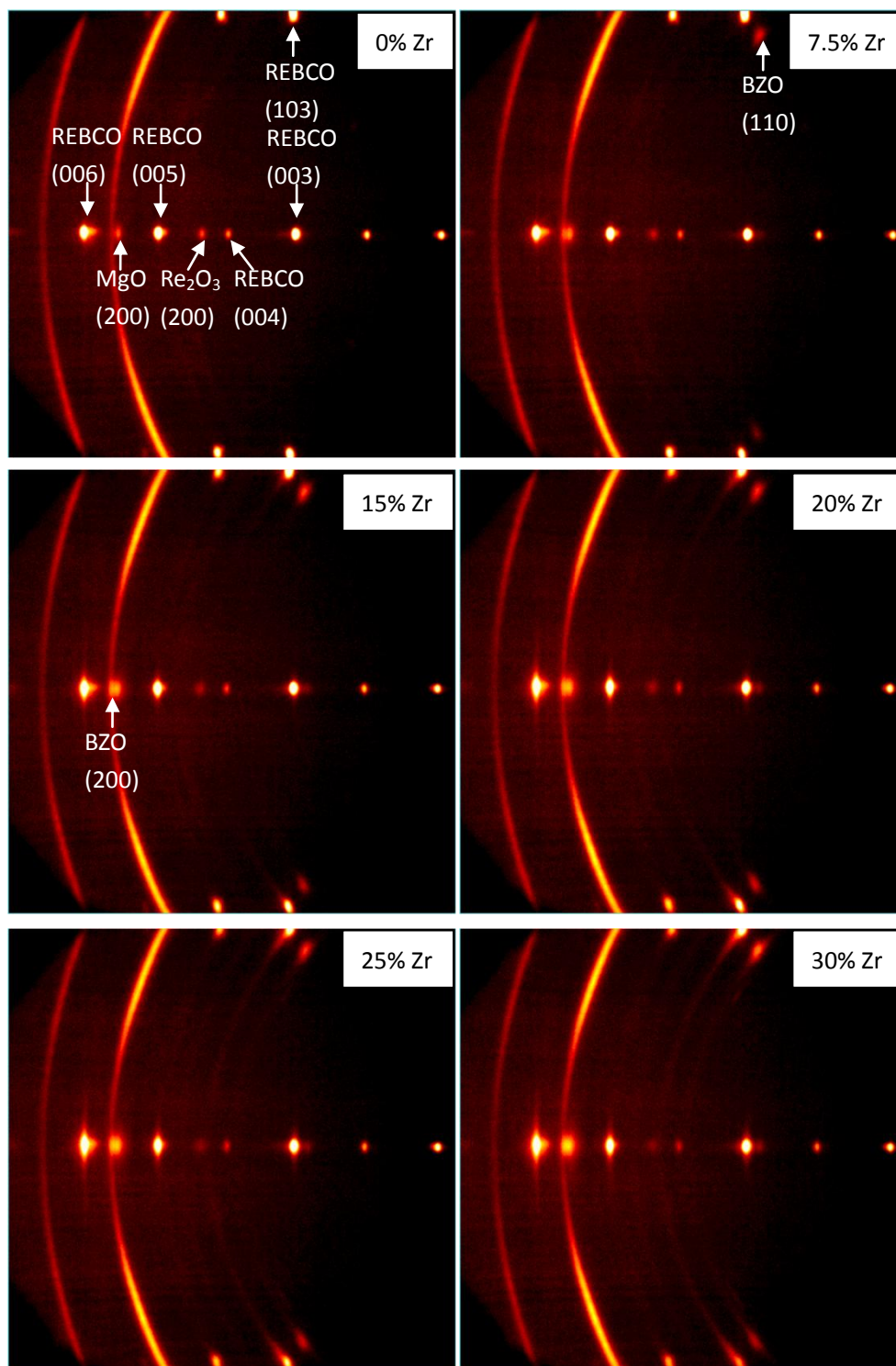


Fig. 3-9 2D x-ray diffraction patterns of GdYBCO superconducting tapes with 0%–30% Zr addition.

As shown in Figure 3-9, with increasing Zr doping level, (103), (005) and (006) peaks of GdYBCO become broader. Rings start to appear around these peak positions in 15% Zr-doped sample. It is clear that the structural quality of GdYBCO films is degraded with increasing Zr content above 15%, which matches with the drop in self field critical current from 15% Zr doping level onwards as previously illustrated in Figure 3-3. It is also found that increasing Zr doping level leads to weaker RE_2O_3 (200) peak, which means the content of RE_2O_3 is decreasing with higher Zr doping level.

All the samples with Zr addition display BZO (110) peak, which confirms that in this work BZO is always formed in the GdYBCO films no matter how much Zr doping level is added. Although the BZO (200) peak has a close location to the MgO (200) peak which was from the buffer layer, it is still observed especially in samples with 15% Zr doping level and higher.

Theta-2theta XRD characteristics of samples with 15, 20, 25 and 30% Zr doping in the vicinity of BZO (200) and GdYBCO (006) are shown in Figure 3-10. As shown in Figure 3-10, BZO (200) peak shows stronger intensity with increasing Zr doping level from 15% to 30%. It confirms that the additional Zr even up to 30% in the precursor is still resulting in more BZO.

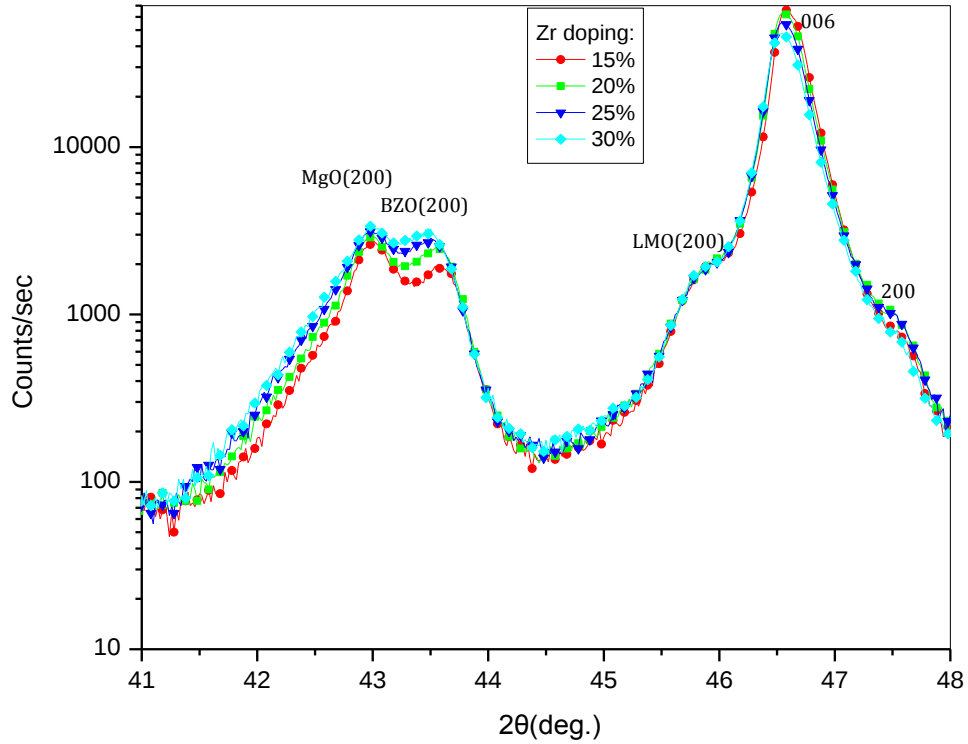


Fig. 3-10 XRD θ - 2θ scans in the vicinity of BZO (200) and (GdY)BCO (006) of GdYBCO films with 15%–30% Zr doping.

Figure 3-11 shows the surface microstructure of samples with 15, 20, 25 and 30% Zr doping levels. It is found that GdYBCO matrix remains relative smooth and dense even at high Zr doping levels. Needle-shaped secondary phases appear in these Zr doped samples, mainly along the length and width directions (a-axis and b-axis). The size of needle-shaped secondary phases increases with increasing Zr addition from 15% to 25%, then remain at the same size from 25 to 30%. The density of these secondary phases follows the contrary tendency in that it varies slightly from 15 to 25%, increases sharply from 25% to 30%. The formulation and enlargement of secondary phases in high Zr doping level may be responsible to the degradation of GdYBCO film quality.

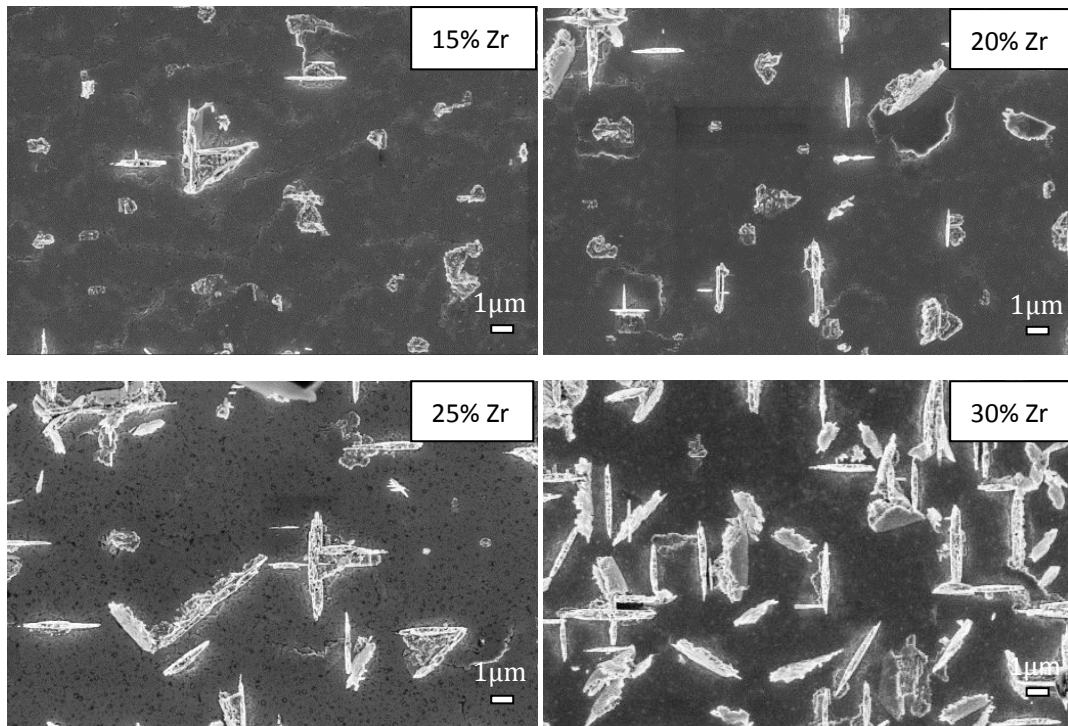


Fig. 3-11 Surface microstructure of GdYBCO films with 15%–30% Zr doping.

Figure 3-12 shows plan-view microstructure of GdYBCO films with 7.5%, 15%, and 20% Zr doping levels obtained by TEM. It is found that from 7.5% to 20% Zr doping the average size of BZO nanorods remains fairly constant at about 5 nm. In 7.5% Zr doped sample, the distribution of BZO nanorods is not uniform, with a wide range of BZO nanorods spacing. The distances between BZO nanorods in 15% and 20% Zr doped samples are similar, about 20 nm. The spacing of BZO nanorods is found to reach to a minimum limit at a Zr doping level of 15%.

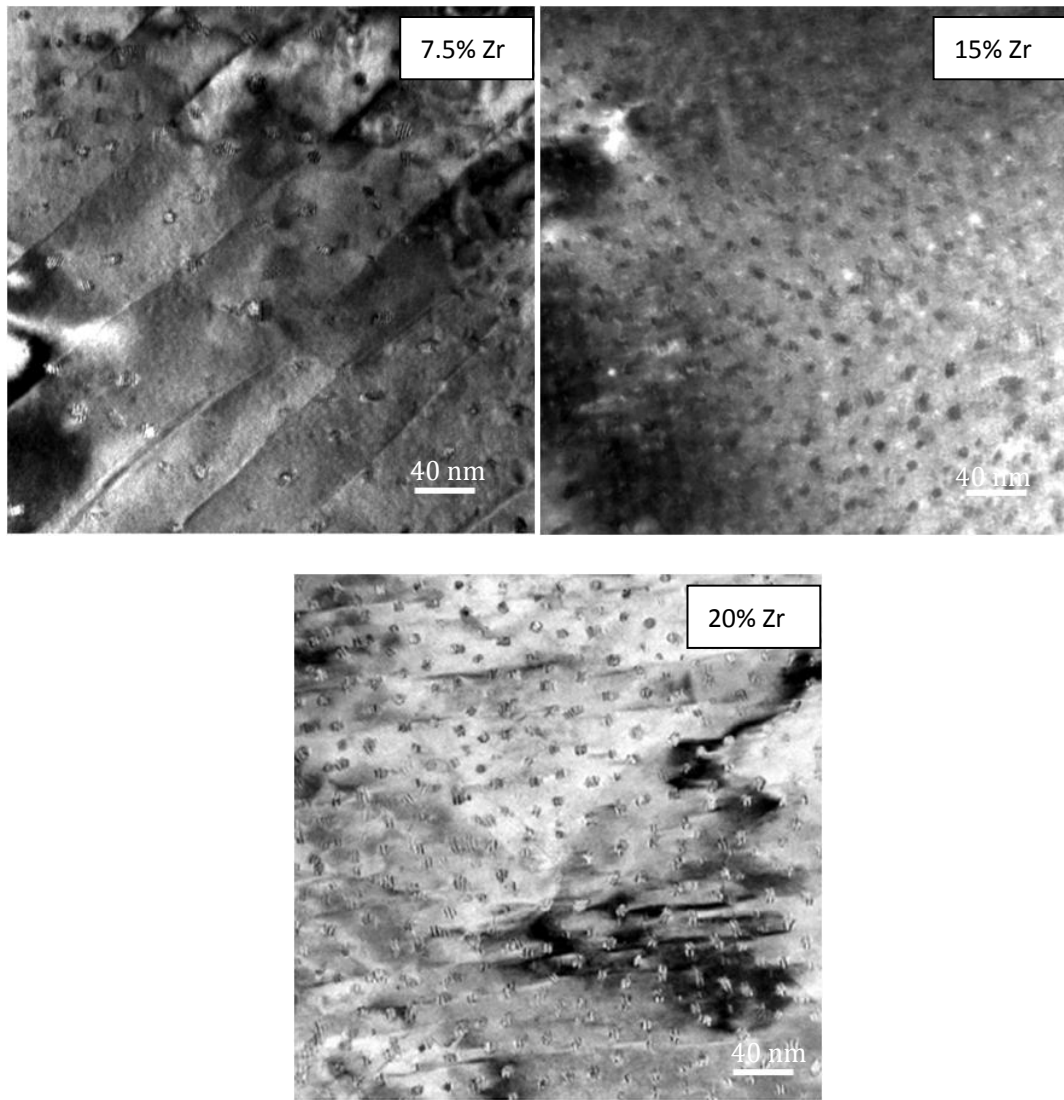


Fig. 3-12 TEM plan-view microstructure of GdYBCO films with 7.5%, 15%, and 20% Zr doping level.

Considering that the XRD results show that increasing Zr from 15% to 20% results in more BZO in the film, it appears that at Zr doping levels above 15%, BZO forms in configurations other than c-axis-aligned nanorods. Figure 3-13 shows a cross-section TEM image of 25% Zr doped GdYBCO film. As shown, a high density of BZO nanorods grow continuously along the c-axis from the buffer to the film surface, which can provide effective pinning effect when the magnetic field parallel to c-axis.

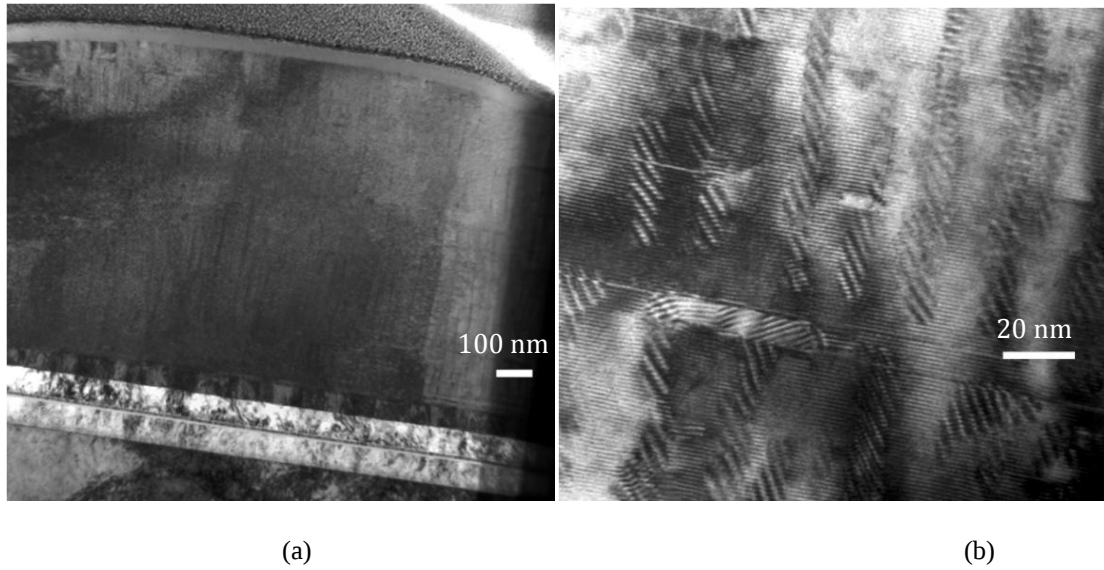


Fig. 3-13 TEM cross-section microstructure of GdYBCO films with 25% Zr doping level.

In figure 3-13(b), some in-plane BZO defects about 40 nm long are observed in the film, interrupting the continuous growth of c axis aligned BZO nanorods. The existence of in-plane BZO defects explains that increasing Zr addition level above 15% does not lead to the obvious changes in the distribution of c-axis aligned BZO columns even though there is more BZO content in the film. It has been shown in reference [42] that the size and volume fraction of in-plane BZO defects increase with the increase of Zr doping level. It is considered that at low Zr doping levels, c-axis BZO nano columns dominate in the film while in-plane BZO defects are not obvious. At a high Zr doping level, it is possible that the size and spacing of BZO nano columns increase to a saturated limit, then BZO starts to grow in the ab plane and play a significant effect on interrupting continuous growth of c-axis aligned BZO nanorods, causing a decrease on the pinning effect and hence the in-field critical current.

In summary, some conclusions could be obtained from the microstructure study of GdYBCO films with high Zr doping level:

1. Increasing Zr doping level from 0% to 30% causes the quality degradation of GdYBCO and more BZO in the film.
2. More needle-shaped secondary phases are observed on the surface of GdYBCO tapes with higher Zr addition.
3. The distribution spacing of BZO nanorods reach the saturated limit with increasing Zr doping level to 15%.
4. In-plane BZO defects about 40 nm long are observed, interrupting the continuous growth of c axis aligned BZO nanorods in films with high Zr content.

3.4 Relationship between composition and 30K, 3T electromagnetic properties of Zr-doped REBCO films

The complex triangular relationship among film electromagnetic properties (zero field critical current, in-field performance), film characteristics (structure, composition), and process condition in MOCVD (precursor recipe, deposition temperature and deposition rate) is very instructive and important for improving the performance of Zr-doped GdYBCO. In the previous work, Zr addition dependence of in-field performance has been investigated. Considering that the variation in content of other elements (Gd, Y, Ba, Cu) in films could be associated with in-field performance just as Zr is, it is necessary to figure out the relationship between film composition and electromagnetic properties of Zr doped GdYBCO film.

The composition of Zr-doped GdYBCO film is made up of five cations: the individual element content of barium, zirconium, copper, yttrium and gadolinium. The sum of the content of yttrium and gadolinium is considered as one parameter since they play a similar role in the GdYBCO lattice and are almost at a equal amount in the film. By this way, the independent variables become the content of barium, zirconium, copper and the sum of the content of yttrium and gadolinium.

Since quadrupling superconductor performance at 30 K, 2.5 T for commercialization of 10 MW wind generators is the major aim of our recent funded project, the lift factor at 30K, 3T and minimum critical current at 30K, 3T of 29 Zr doped GdYBCO samples are studied in this work. Since film composition is mainly controlled by precursor composition, the precursor composition information of 29 involved samples is shown as follows.

In Table 3-1, it was shown that the precursor molar ratio of Gd: Y: Ba: Cu is kept as 0.6: 0.6: 2: 2.3. As shown in Figure 3-14, two Gd or Y molar compositions 0.55 and 0.6, Ba molar composition of 2 and 2.15, three Cu molar compositions of 2.1, 2.2, and 2.3 were used in the 29 samples studied. Zr doping level was changed from 7.5% to 20%.

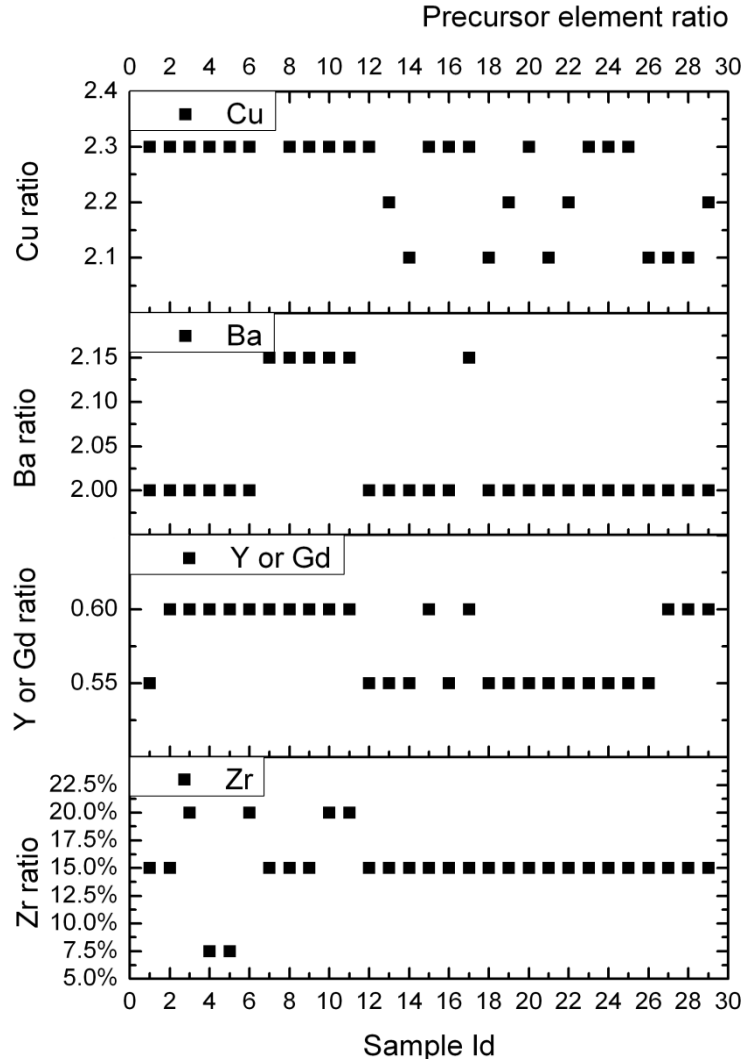


Fig. 3-14 Precursor molar composition of Zr doped GdYBCO films studied.

A ternary diagram is used for displaying the relationship and tendency between electromagnetic properties of Zr doped GdYBCO film and composition with four different axis combinations — (Ba, Zr, Cu), (Ba, Cu, Gd+Y), (Ba, Gd+Y, Zr) and (Cu, Zr, Gd+Y). As mentioned earlier, lift factor refers to the ratio of critical current at $H||c$ at any given temperature and magnetic field to 77K self-field critical current. The relationship between element molar composition and 30K, 3T lift factor of Zr-doped GdYBCO films is shown in Fig. 3-15.

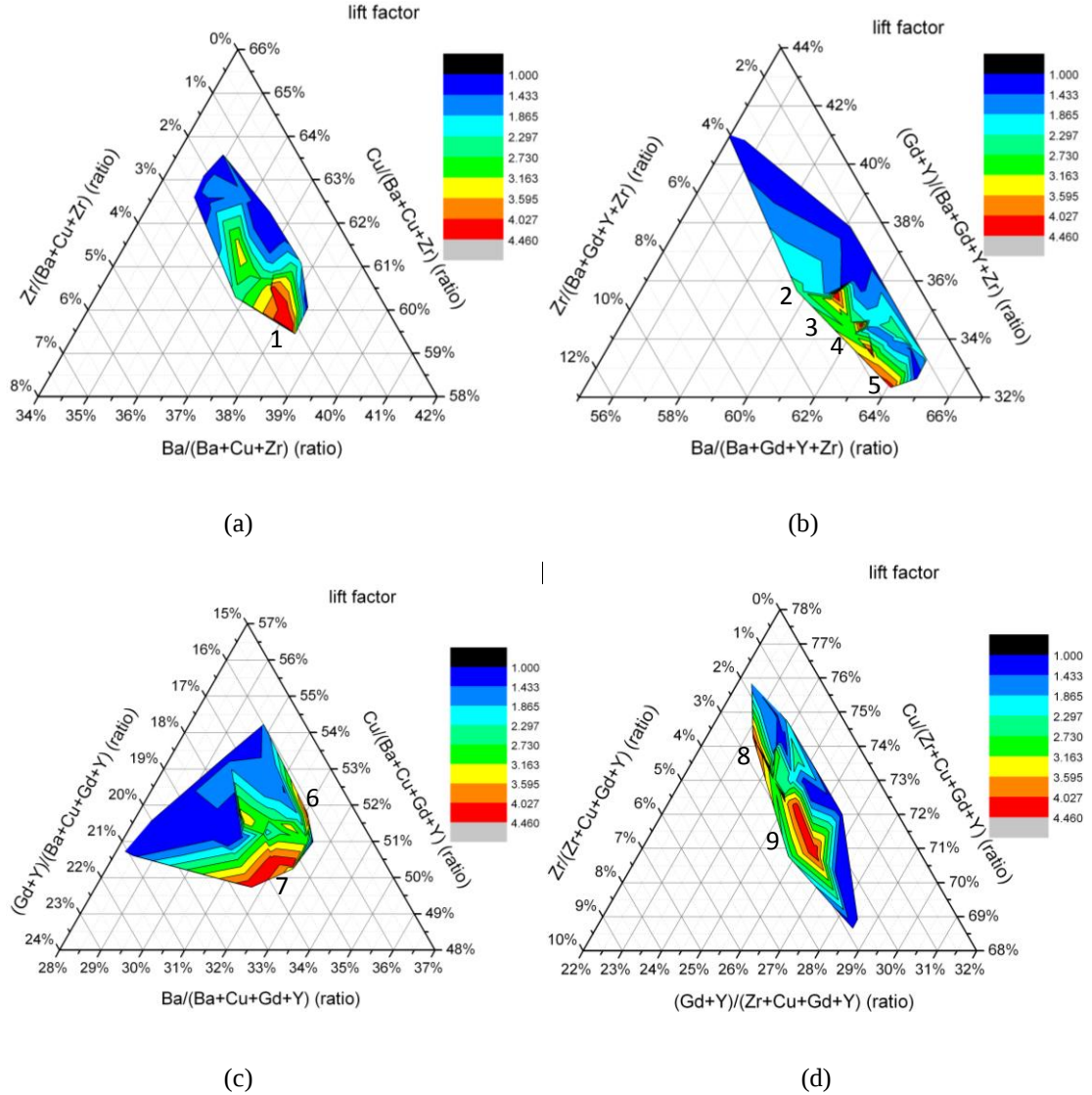


Fig. 3-15 Ternary diagrams showing influence of film composition on 30K, 3T lift factor of Zr-doped GdYBCO films.

It is found in Fig. 3-15(a) that a higher Ba and less Cu in the film is preferable to enhance lift factor at 30K, 3T, reaching the maximum lift factor at Zr: Ba: Cu = 2: 38: 60. In Fig. 3-15(b), it is observed that with Ba, Gd+Y and Zr axes, the region with highest lift factor disperses to four smaller regions: Region 5 with the largest area of highest lift factor at around Ba: (Gd+Y): Zr = 3.5: 64: 32.5 and Region 2 with the second largest area at about Ba: (Gd+Y): Zr = 3.5: 61: 35.5. As shown in Fig. 3-15(c), it is found that the lift factor at 30K, 3T increases with increasing Ba content. In

addition, Region 6 with the lowest Gd+Y content at Ba: Cu: (Gd+Y) = 32: 52: 16 occupies a very small area of the highest lift factor compared with Region 7 at around Ba: Cu: (Gd+Y) = 32: 50: 18. Similar to Figure 3-15(c), two red regions are found in Figure 3-15(d) — Region 8 with smaller area of the highest lift factor at (Gd+Y): Cu: Zr = 23.2: 74.3: 2.5, Region 9 with larger area at the ratio of (Gd+Y): Cu: Zr varying from 26.5: 71: 2.5 to 25: 72.5: 2.5.

Comparing the area of regions with lift factor above 4 is helpful to locate the optimal composition for the highest lift factor (above 4). By tracking the sample information shown in Table 3-2, it is found that Region 5, Region 6 and Region 8 come from the same sample No. 16. Since region 6 and region 8 have much smaller area, the composition of No. 16 is not preferable to be treated as the optimal composition for high lift factor.

Table 3-2 Film composition and located regions of Zr-doped GdYBCO films studied with lift factors above 4.

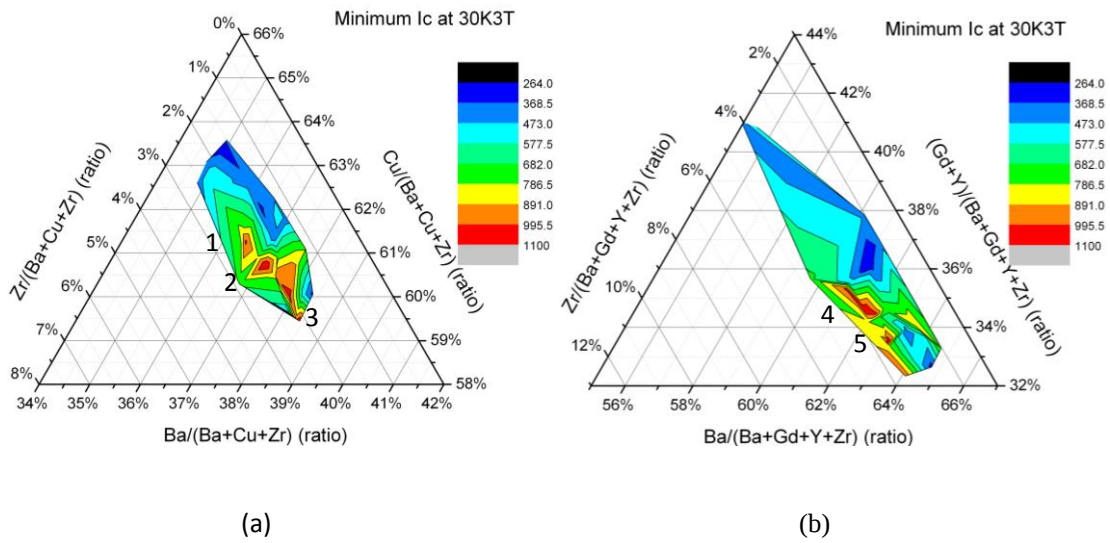
Sample ID	Zr content (%)	(Gd+Y) content (%)	Ba content (%)	Cu content (%)	Regions located in Fig. 3-15	Lift factor
13	1.79537	16.94103	31.82046	49.44313	1,4,7,9	4.42319
14	1.8447	18.18742	31.15433	48.81355	1,2,7,9	4.45088
15	1.69174	17.38789	31.34984	49.57053	1,3,7,9	4.39365
16	1.74838	15.88498	31.4871	50.87954	1,5,6,8	4.24565

Among samples 13, 14, and 15, it is found that Region 2 has a larger area compared with regions 3 and 4. So the composition located in Region 2 is more preferable to be chosen as the optimal composition.

As shown in Table 3-2, the sample compositions of Region 1, Region 2, Region 7 and Region 9 could be associated with the same sample No. 14, whose film composition is 1.8% Zr, 18.2% Gd+Y, 31.2% Ba, and 48.8% Cu. This composition is equivalent to Zr: (Y+ Gd): Ba: Cu = 0.115: 1.16: 2: 3.13 and is considered to be the optimal film composition for the highest lift factor.

The relationship between element molar composition and minimum critical current Zr-doped GdYBCO films at 30K, 3T is shown in Fig. 3-16. Compared with Fig. 3-15, it is found that in Fig. 3-16 the regions with minimum critical current above 900 A occur at almost the similar positions and shapes as the regions with lift factor higher than 4.

As shown in Fig. 3-16(a), (b), (c) and (d), regions 3, 4, 6 and 7 should correspond to the optimal composition of minimum critical current at 30K, 3T according to the distribution tendency and the area of regions.



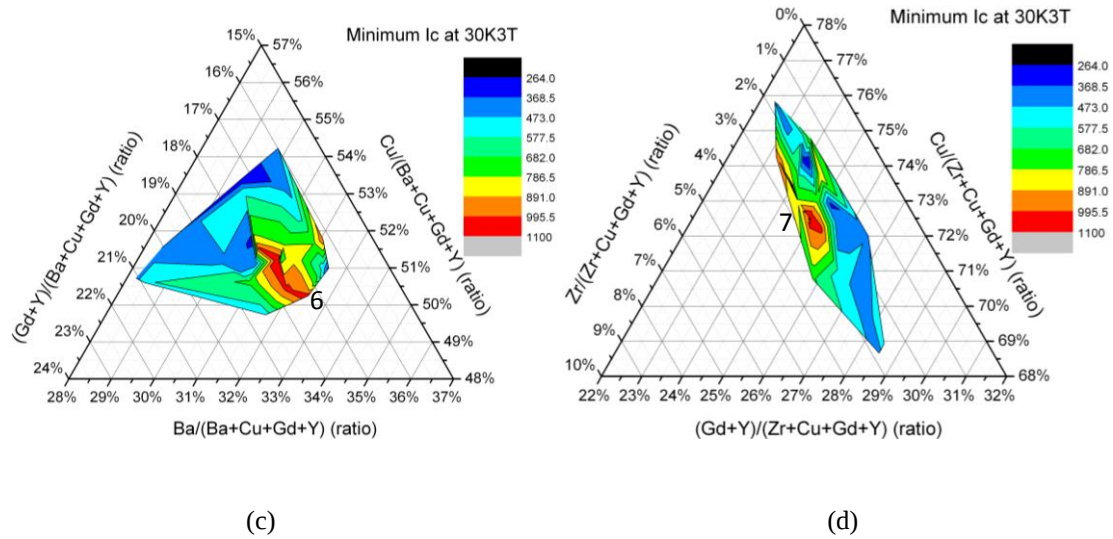


Fig. 3-16 Ternary diagram showing the influence of film composition on the minimum critical current at 30K, 3T of Zr-doped GdYBCO films.

From the information shown in Table 3-3, it is found that regions 3, 4, 6 and 7 come from the same sample No. 15, with composition as 1.7% Zr, 17.4% Gd+Y, 31.3% Ba, and 49.6% Cu, which is equivalent to Zr: (Y+Gd): Ba: Cu = 0.109: 1.11: 2: 3.17.

Table 3-3 Film composition and regions located of Zr-doped GdYBCO films studied with minimum critical current above 1000 A/12 mm.

Sample ID	Zr content (%)	(Gd+Y) content (%)	Ba content (%)	Cu content (%)	Regions located in Fig. 3-16	Minimum critical current
3	1.76545	16.9724	31.90422	49.35793	3,5,6,7	1079
9	1.88764	17.45925	30.08897	50.56413	1,4,6,7	1016
15	1.69174	17.38789	31.34984	49.57053	3,4,6,7	1024
28	1.79372	17.19837	30.72533	50.28258	2,4,6,7	1100

The compositions of the 29 Zr-doped GdYBCO samples studied are shown in Fig. 3-17. The blue line marks the optimal composition for the highest lift factor at 30K, 3T and the red line displays the optimal composition for the highest minimum

critical current at 30K, 3T. It is seen that the optimal compositions for the highest lift factor at 30K, 3T and for the highest minimum critical current at 30K, 3T are almost the same. From Fig. 3-17, it is found that a high barium and a low copper composition could result in a high lift factor and a high minimum critical current at 30K, 3T.

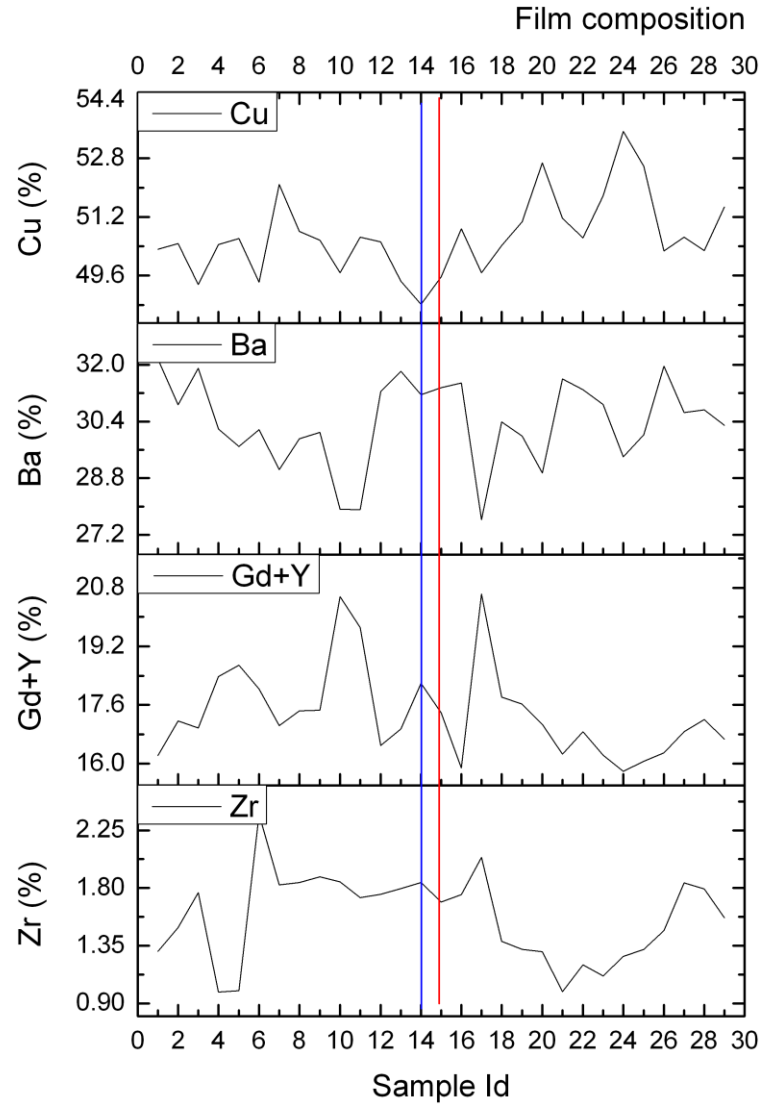


Fig. 3-17 Film compositions of all 29 Zr doped GdYBCO samples studied. The blue line shows the optimal composition for the highest lift factor at 30K, 3T and the red line shows the optimal composition for the highest minimum critical current at 30K, 3T.

Chapter 4 Summary and Conclusions

In order to apply Zr-doped GdYBCO superconducting tapes in coil-based application such as wind generators and motors, the MOCVD process has been optimized to obtain higher self-field critical current at 77K at different Zr doping levels. The self-field critical current at 77K of GdYBCO with Zr doping level above 15% has been improved significantly.

After the MOCVD process optimization, the angular dependence and field dependence of GdYBCO tapes with Zr doping level from 7.5% to 30% have been investigated at temperatures from 40K to 77K and magnetic field from 0T to 5T. 20% Zr doping is found to be the optimal doping level with the highest minimum critical currents and the highest critical currents at $H \parallel c$ over a wide range of temperatures and magnetic fields and especially at low temperature and high magnetic field, which is different from the optimum doping level at low fields and 77 K. At 77K, 1T, 7.5% Zr doping is still the optimal Zr doping level but 15% and 20% Zr doping are equally good as well. At 40K and 50K, 15%, 20% and 25% Zr doping level shows better in-field performance than 7.5% Zr doping. At magnetic fields above 3T, 15%, 20%, 25% and 30% Zr doping levels are found to be superior to 7.5% Zr doping.

The microstructure of GdYBCO with Zr doping level from 7.5% to 30% has been studied systematically. Increasing Zr doping level causes a continuous quality degradation of GdYBCO, formation of more BZO and less RE_2O_3 in the film. The spacing of c-axis aligned BZO nanorods decreases to a minimum level at 15% Zr doping level. As Zr doping is increased above 15%, in-plane BZO defects forms in

the film, interrupting the continuous growth of c-axis-aligned BZO nanorods.

For developing high performance Zr-doped GdYBCO tapes for 10 MW wind generators, the influence of composition on in-field performance has been studied to find out the optimal film composition with the best in-field performance at 30K, 3T. The optimal compositions for the highest lift factor at 30K, 3T and the highest minimum critical current at 30K, 3T have been found to be close to each other: 1.8% Zr, 18.2% Gd+Y, 31.2% Ba, and 48.8% Cu for the highest lift factor; 1.7% Zr, 17.4% Gd+Y, 31.3% Ba, and 49.6% Cu for the best for minimum critical current at 30K, 3T. It is also found that high barium and low copper in the film are preferable to obtain the highest high lift factor and the highest minimum critical current at 30K, 3T.

Future work could be focused on the following aspects:

1. Precise susceptor temperature optimization for 15%, 20%, 25% and 30% Zr doping levels.
2. Selecting more samples with dispersed wide range of compositions to repeat the composition analysis associated with in-field performance. Extend this analysis to other temperatures and magnetic fields.
3. Building the connection between process parameters and film composition to construct the triangle relationship among process condition, film composition and in-field performance.

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