IEEE/CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), October 2016.
ASC 2016 paper 4MPo2A-01. ASC Alexander Shikov Memorial Prize Winner.
DOI: 10.1109/TASC.2017.2660768



# MOCVD of High Zr-Doped HTS Coated Conductors

M. Heydari Gharahcheshmeh[1], E. Galstyan[1], A. Xu[1], J. Kukunuru[1], R. Katta[1], Y. Zhang, [1] G. Majkic[1], X. Li[1], V. Selvamanickam[1]

[1]Department of Mechanical Engineering and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-4006, USA

***Abstract*— The conditions for achieving high in-field critical current densities ($J_C$) above 20 MA cm$^{-2}$ at 30 K, 3T (B||c) in $REBa_2Cu_3O_{7-\delta}$ (REBCO and RE=Gd, Y) superconductor tapes with Zr content of 25 mol.% have been determined. In this work, heavily-doped $(Gd,Y)Ba_2Cu_3O_{7-\delta}$ superconductor tapes with 25 mol.% Zr addition were fabricated by Metal Organic Chemical Vapor Deposition (MOCVD) using a reel-to reel process. The optimal chemical compositional range of $(Gd,Y)Ba_2Cu_3O_{7-\delta}$ superconductor tapes with Zr content of 25 mol.% obtained by Inductive Coupled Plasma–Mass Spectrometry (ICP-MS) to achieve the critical current densities above 3.5 MA cm$^{-2}$ at 77K in zero applied magnetic field has been determined. The superconducting transition width ($\Delta T_c$) as narrow as 0.4 K and the onset critical transition temperature ($T_c$-onset) as high as 92 K were obtained in the 25 mol.% Zr-added (Gd,Y)BaCuO superconductor tapes.**

## I. Introduction

SECOND-GENERATION (2G) of High Temperature Superconductors (HTS) based on epitaxial $REBa_2Cu_3O_{7-\delta}$ (RE = rare earth elements, REBCO) films are suitable for use in various electric power applications such as power cables, generators, and high energy particle accelerators [1]-[6].

The in-field transport performance of REBCO films has been significantly enhanced by introducing Artificial Pinning Centers (APCs), such as $BaZrO_3$ (BZO) [1]-[8], $BaHfO_3$ (BHO) [4], [9], $BaSnO_3$ (BSO) [10], [11], $BaNb_2O_6$ (BNO) [12], $Y_2BaCuO_5$ [13], and $Gd_3TaO_7$ [14].

Previously, most of the reports were based on the dopant levels of less than 10 mol. % in REBCO films, which do not display exemplary performance in the temperatures less than 50 K and in moderate-to-high applied magnetic fields. Using high levels of Zr addition, up to 25 mol.% Zr, $J_c$ values above 20 MA cm$^{-2}$ at 30 K, 3T (B||c) in (Gd,Y)BCO superconductor tapes have been achieved by our group [5]. Still, improving the lift factor (ratio of $J_c$ at 30 K, 3 T (B||c) to the $J_c$ at 77 K, 0T) without deteriorating the $J_c$ at 77 K in zero applied magnetic field is the major challenge in heavily doped Zr added (Gd,Y)BCO films.

In this paper, the optimal compositional range of (Gd,Y)BCO superconductor tapes with Zr content of 25 mol.% to achieve the critical current densities above 3.5 MA cm$^{-2}$ at 77 K in zero applied magnetic field has been determined. The effect of chemical composition on the superconducting transition width ($\Delta T_c$) as well as the onset critical transition temperature ($T_c$-onset) in 25 mol.% Zr-added (Gd,Y)BCO superconductor tapes have been studied.

## II. Experiment

A reel-to-reel MOCVD system was used to deposit (Gd,Y)BCO superconductor tapes with 25 mol.% Zr addition. The precursor was made by mixing the organometallic tetramethyl heptanedionate (thd) compounds of Zr, Gd, Y, Ba, and Cu in Tetrahydrofuran (THF) solvent at appropriate molar concentration. The substrate used in this study was Hastelloy C-276, with the buffer configuration of; $Al_2O_3/Y_2O_3$/IBAD-MgO/MgO/$LaMnO_3$. (Gd,Y)BCO films with 25 mol.% Zr addition were fabricated at a deposition rate of ~ 80 nm min$^{-1}$. The thickness of films was about 0.9-1.1 μm and controlled by tape speed.

The compositions of Zr added (Gd,Y)BCO films were determined by Inductive Coupled Plasma–Mass Spectrometry (ICP-MS). The transport critical current of films was determined by the standard four-probe method using a 3 μV cm$^{-1}$ criterion. The superconductive transition temperatures ($T_c$) were determined by a magnetic induction using a lock-in amplifier. High Resolution X-ray Diffraction (HRXRD), and Transmission Electron Microscope (TEM) studies were performed to study the microstructure of the Zr added (Gd,Y)BCO films.

## III. Results and Discussion

The critical current density ($J_c$) values at 77 K in zero applied magnetic field as a function of (Ba+Zr)/Cu atomic fraction ratio of 104 (Gd,Y)BCO tapes with 25 mol.% Zr addition are shown in Fig. 1. The incorporation of BZO in (Gd,Y)BCO tapes was 10 vol.%. It is observed that with increase in (Ba+Zr)/Cu atomic fraction ratio in the films from 0.57 to 0.69, the self-field Jc at 77 K increases. However, as the (Ba+Zr)/Cu content further increases from 0.69 to 0.85, self-field $J_c$ decreases from 4 MA cm$^{-2}$ to 0.5 MA cm$^{-2}$. The (Ba+Zr)/Cu content of the 25 mol.% Zr-added (Gd,Y)BCO tapes should be in the range of 0.69 and 0.71 for a self-field $J_c$ at 77 K above 3.5 MA cm$^{-2}$.

All 25 mol.% Zr-added (Gd,Y)BCO tapes have been fabricated by constant nominal precursor ratio of rare-earth. The formation of CuO particles on the surface and a noticeable amount of a-axis grains in Zr-added (Gd,Y)BCO tapes with excess Cu, (Ba+Zr)/Cu content less than 0.69, lead to drop in self-field $J_c$ at 77 K as can be seen in Fig. 1. The self-field $J_c$ values below than 1 MA cm$^{-2}$ in heavily doped Zr-(Gd,Y)BCO tapes are mainly due to the presence of a-axis grains and a large amount of secondary phases.

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As can be seen in the Fig. 2, the $\Delta T_c$ decreases from 2.5 to 0.4 K with increasing (Ba+Zr)/Cu atomic fraction ratio of the films from 0.56 to 0.69, and then increases for higher values of (Ba+Zr)/Cu content. The optimum range of (Ba+Zr)/Cu content for the lowest $\Delta T_c$ is shown by dashed line in Fig. 2, which matches the ideal range of the film's chemical composition for achieving the highest self-field $J_c$ at 77 k for heavily doped Zr-added (Gd,Y)BCO films as shown in Fig. 1. The narrow transition widths should be a response of high homogeneity in composition and absence of the secondary phases and a-axis grains.

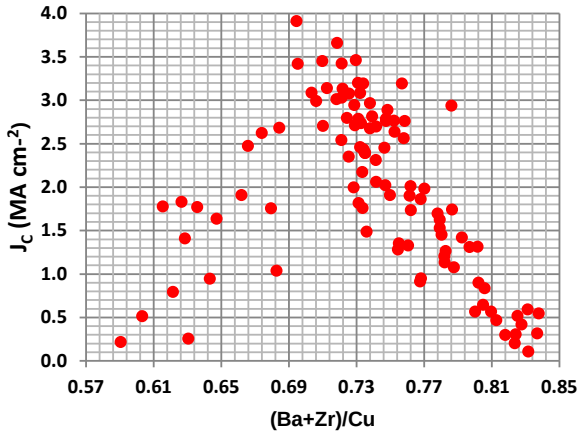


Fig. 1. The self-field critical current density ($J_c$) at 77 K of 104 (Gd,Y)BCO tapes with Zr content of 25 mol.% as a function of (Ba+Zr)/Cu atomic fraction ratio.

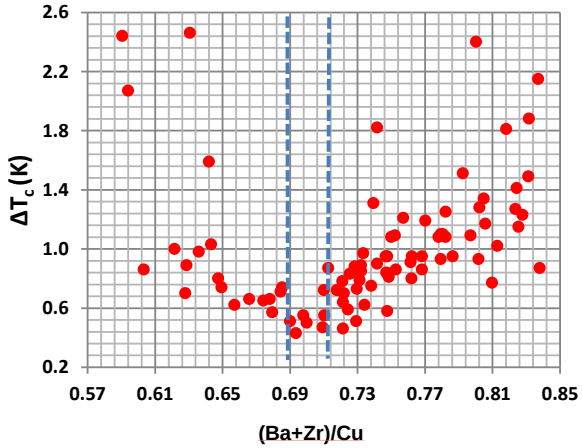


Fig. 2. The superconducting transition width ($\Delta T_c$) as a function of the (Ba+Zr)/Cu atomic fraction ratio of 25 mol.% Zr-added (Gd,Y)BCO tapes.

It is noticed, according to Fig. 3, that with increase in Cu/(Ba+Zr+Y) content of tapes, the $T_c$-onset increases. However, as Cu/(Ba+Zr+Y) content further increases from 1.17 to 1.33, the $T_c$-onset decreases by approximately 3 K. It is observed that most of heavily doped Zr-added (Gd,Y)BCO superconductor tapes exhibit $T_c$-onset higher than 90 K. The decrease of $T_c$-onset below than 90 K in heavily doped Zr-added (Gd,Y)BCO tapes with Cu/(Ba+Zr+Y) content of lower than 1 and higher than 1.24 may be due to the formation of large amount of oxide particles and noticeable amount of a-axis grains, respectively.

$T_c$ reduction is mainly attributed to the charge transfer from the conducting $CuO_2$ plane to Cu-O chain which decreases the carrier concentration [15], [16]. A large amount of cation disorder in heavily-doped Zr-added (Gd,Y)BCO tapes can cause variation in the carrier concentration.

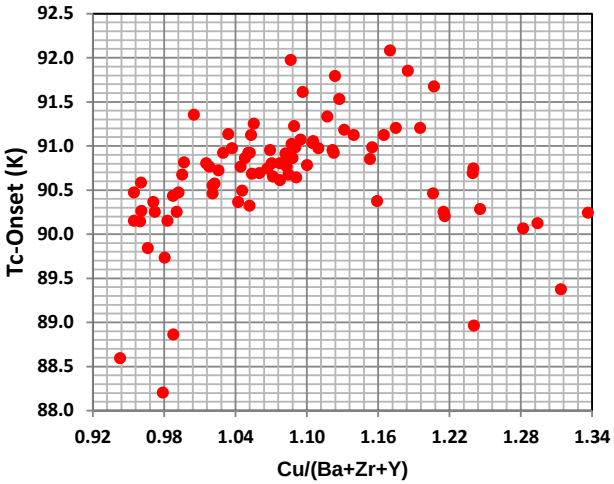


Fig. 3. The onset critical transition temperature ($T_c$-onset) as a function of Cu/(Ba+Zr+Y) atomic fraction ratio of 25 mol.% Zr-added (Gd,Y)BCO tapes.

It was found previously by our group that a lift factor (ratio of $J_c$ at 30 K, 3 T (B||c) to the self-field $J_c$ at 77 K) above 6 could be achieved in the films with (Ba+ Zr)/Cu content above 0.71 [5]. Fig. 2, and Fig. 3 show with modifying the process parameters of the MOCVD, even at (Ba+ Zr)/Cu content as high as 0.8, a $\Delta T_c$ as narrow as 1.4 K and high $T_c$-onset above 90 K can be achievable which has been proven to be difficult by other deposition methods. If the self-field $J_c$ values at 77 K can be increased at these high levels of (Ba+ Zr)/Cu, excellent in-field performance could be attained over a wider composition window using the heavily-Zr-added (Gd,Y)BCO superconductor tapes.

The HRXRD and TEM results will be discussed in details in the final version of this manuscript.

## IV. Conclusion

The optimal composition range of 25 mol.% Zr-added (Gd,Y)BCO superconductor tapes has been determined by ICP-MS. It was found that (Ba+Zr)/Cu atomic fraction ratio of (Gd,Y)BCO tapes with 25 mol.% Zr addition should be in the range of 0.69 and 0.71 to achieve the $J_c$ above 3.5 MA cm$^{-2}$ at 77 K, 0T. Self-field $J_c$ values below than 1 MA cm$^{-2}$ in tapes with (Ba+Zr)/Cu below 0.65 and above 0.8 are attributed to the presence of a-axis grains and a large amount of secondary phases. With modifying the process parameters in MOCVD, $\Delta T_C$ as sharp as 0.4 K was obtained in 25 mol.% Zr-added (Gd,Y)BCO films with (Ba+Zr)/Cu content of 0.69. $T_c$-onset values above 90 K over a wide range of Cu/(Ba+Zr+Y) atomic fraction ratio from 1 to 1.24 were obtained in heavily-doped Zr-added (Gd,Y)BCO tapes.

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