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Tb AND Ce DOPED Y123 FILMS PROCESSED BY PULSED LASER DEPOSITION

Joseph W. Kell, Timothy J. Haugan, Mary Frances Locke, and Paul N. Barnes

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14. ABSTRACT
To evaluate possible flux pinning enhancement in $YBa_2Cu_3O_{7-x}$ (Y123) films due to partial rare-earth ion substitutions, Ce and Tb doping are studied. Bulk ceramic targets of varying compositions ($Y_{1-x}RE_xBa_2Cu_3O_{7-x}$) were made with several doping levels (x = 0 001 to 0.1, RE = Ce or Tb) by using regular solid-state reaction and sintering procedures. These targets were used to deposit Ce and Tb doped YBCO films onto $SrTiO_3$ single crystal substrates by pulsed laser ablation. Doped YBCO films were characterized for Tc, magnetic field dependence of J_c (at 77 K), microstructure, and other properties. The results are compared to undoped YBCO films processed in similar manner.

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Tb and Ce Doped Y123 Films Processed by Pulsed Laser Deposition

Joseph W. Kell, Timothy J. Haugan, *Member, IEEE*, Mary Frances Locke, and Paul N. Barnes

***Abstract*—To evaluate possible flux pinning enhancement in $YBa_2Cu_3O_{7-z}$ (Y123) films due to partial rare-earth ion substitutions, Ce and Tb doping are studied. Bulk ceramic targets of varying compositions ($Y_{1-x}RE_xBa_2Cu_3O_{7-z}$) were made with several doping levels ($x = 0.001$ to 0.1, $RE = Ce$ or Tb) by using regular solid-state reaction and sintering procedures. These targets were used to deposit Ce and Tb doped YBCO films onto $SrTiO_3$ single crystal substrates by pulsed laser ablation. Doped YBCO films were characterized for T_c, magnetic field dependence of J_c (at 77 K), microstructure, and other properties. The results are compared to undoped YBCO films processed in similar manner.**

***Index Terms*—High-temperature superconductors, magnetic field measurement, superconducting materials, thin films.**

I. Introduction

COATED conductors using biaxially aligned $YBa_2Cu_3O_{7-\delta}$ (Y123) on buffered metallic substrates have been shown to have high critical current densities $(J_c) > 10^6$ A/cm^2 and good flux pinning characteristics in applied magnetic fields [1]–[3]. As such, Y123 has great promise as a second generation high temperature superconducting (HTS) wire for use in generators and motors as well as in other important electrical devices [4]–[6]. However, when magnetic fields are applied parallel to the c-axis, J_c tends to decrease one to two orders of magnitude when fields of between 1 T and 5 T are applied [7], [8]. This shows that further improvement of J_c is desired, especially when subjected to high magnetic fields in the c-axis orientation. This is especially important when a reduction of system weight and size is desired, e.g. superconducting generators and motors. It is also important to increase J_c since the upper design limit of the magnetic field for a given coil design is generally based upon the value of $J_c(H)$.

One way to improve the flux pinning characteristics of type-II superconductors is to introduce secondary superconducting phases into the material [1]–[3]. Since Y123 and other RE123 materials have similar structures, this can be accomplished by substituting other rare earth elements for yttrium in Y123 films. However, only a few of the rare earth elements have been shown to not form a pure RE123 phase. In this work, two of these elements, Tb and Ce, are used to substitute for Y in Y123 thin films. Both have been noted in the literature as not forming the RE123 phase, at least in bulk powders [9]. Both of these elements are divalent, having both +3 and +4 valence states. These states will possibly allow the two elements to act as pinning sites by alternate chemical bonding. Assuming a fully homogenous structure, the size of the pinning particles would approximately be the size of the RE123 unit cell. The nature of pinning could potentially be nonsuperconducting inclusions/sites in addition to or in lieu of strain induced improvements due to slight changes in the unit cell. The possibility of nonsuperconducting locations is reasonable to consider due to the difficulty in forming the RE123 phase with Tb and Ce.

However, Ce and Tb do differ substantially in other properties. Terbium does not degrade the T_c of Y123; in contrast, Ce affects the T_cs of Y123 by substantially lowering them with increasing Ce content in bulk material [10]. In addition, terbium has a similar ionic radius (1.04 Å) to yttrium (1.019 Å), while Ce is significantly larger (1.143 Å). Using small quantities of dopants allows for the same deposition parameters as in high quality Y123 during PLD. This allows for previously optimized O_2 pressures and laser fluences to be used, thereby reducing the processing time and simplifying the depositions.

Since Tb and Ce have these specific differences from the other rare earths, this study focuses on substituting small quantities $(x \leq 0.1)$ of Tb and Ce for Y in Y123 thin films. In so doing, appropriate defect densities of the inclusions will be produced if the inclusions are sufficiently dispersed. Previous studies have focused on substituting large quantities of Tb for Y in Y123 $(x \geq 0.1)$ [10]–[12] and hence lack any noteworthy success.

II. Experimental

The laser ablation targets were manufactured in-house. Three primary powders were prepared with compositions of $YBa_2Cu_3O_{7-x}$, $Y_{0.90}Tb_{0.10}Ba_2Cu_3O_{7-x}$, and $Y_{0.90}Ce_{0.10}Ba_2Cu_3O_{7-x}$ from the precursor powders Y_2O_3, $BaCO_3$, CuO, CeO_2, and Tb_4O_7 powder (all nominally 99.99+% pure). The powders were dried, mixed, and then calcined at 850°C and 880°C. The resultant powder was then used to make targets of compositions $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_{7-x}$, $Y_{0.99}Tb_{0.01}Ba_2Cu_3O_{7-x}$, $Y_{0.999}Tb_{0.001}Ba_2Cu_3O_{7-x}$, $Y_{0.90}Ce_{0.10}Ba_2Cu_3O_{7-x}$, $Y_{0.99}Ce_{0.01}Ba_2Cu_3O_{7-x}$, and $Y_{0.999}Ce_{0.001}Ba_2Cu_3O_{7-x}$ by diluting the initial $(Y_{0.90}, Tb_{0.10})123$ and $(Y_{0.90}, Ce_{0.10})123$ doped powder with Y123. The targets were then fully reacted and sintered at 940°C until they reached a density of >80% theoretical density. The estimated purity of the targets was 99.99+%.

The multiple compositions of (Y,Tb)123 and (Y,Ce)123 films were deposited by pulsed laser deposition, using parameters and

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The authors are with the Air Force Research Laboratory, WPAFB, OH 45433-7919 USA (e-mail: joseph.kell@wpafb.af.mil; timothy.haugan@wpafb.af.mil; mary.locke@wpafb.af.mil; paul.barnes@wpafb.af.mil).

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TABLE I
SUMMARY OF MAGNETIC DATA FOR Tb AND Ce DOPED Y123

Film Composition	Tc (DC Magnetization)	Jc @ 77K and 0.01T Applied Field	Jc @ 65K and 0.01T Applied Field	Jc @ 77K and 2T Applied Field	Jc @ 65K and 2T Applied Field
Y-123	89.2 K	2.23 MA/cm^2	5.87 MA/cm^2	0.140 MA/cm^2	0.78 MA/cm^2
$(Y_{0.999}Tb_{0.001})$-123	88.0 K	3.13 MA/cm^2	9.01 MA/cm^2	0.107 MA/cm^2	1.24 MA/cm^2
$(Y_{0.99}Tb_{0.01})$-123	89.0 K	2.68 MA/cm^2	8.29 MA/cm^2	0.162 MA/cm^2	1.53 MA/cm^2
$(Y_{0.90}Tb_{0.10})$-123	89.5 K	3.43 MA/cm^2	9.54 MA/cm2	0.100 MA/cm^2	0.70 MA/cm^2
$(Y_{0.999}Ce_{0.001})$-123	88.9 K	1.65 MA/cm^2	5.66 MA/cm^2	0.099 MA/cm^2	1.11 MA/cm^2
$(Y_{0.99}Ce_{0.01})$-123	88.5 K	2.10 MA/cm^2	5.44 MA/cm^2	0.056 MA/cm^2	0.59 MA/cm^2
$(Y_{0.90}Ce_{0.10})$-123	84.8 K	0.52 MA/cm^2	2.86 MA/cm^2	0.001 MA/cm^2	0.21 MA/cm^2

conditions optimized previously for Y123 [13]–[15]. The depositions were performed on strontium titanate (STO) and lanthanum aluminate (LAO) substrates with the overall time for film growth being about 20 minutes. The LAO (100) and STO (100) single crystal substrates were ultrasonically cleaned for 2 minutes, using first acetone followed by isopropyl alcohol. Crystalline substrates were provided by the manufacturer epitaxially polished on both sides of the LAO and on one side for STO, and were attached to the heater using a thin layer of colloidal Ag paint. LAO and STO substrates sizes were $\sim 3.2\ \mathrm{mm} \times 3.2\ \mathrm{mm}$ for magnetic $\mathrm{J_c}$ measurements.

Depositions were performed using a Lambda Physik, LPX 305 KrF excimer laser ($\lambda = 248\ \mathrm{nm}$). The laser pulse rate was 4 Hz and the laser fluence was $\sim 3.2\ \mathrm{J/cm^2}$. The target-to-substrate distance was kept at 6 cm for all of the depositions. The background pressure in the chamber was reduced to $< 6 \times 10^{-6}$ Torr prior to depositions. The oxygen pressure during the deposition was 300 mTorr for all targets, as measured with capacitance manometer and convectron gauges within $<10\%$ variation. Oxygen gas (99.999% purity) flowed into the chamber during growth and the oxygen pressure in the chamber was kept constant using a downstream throttle-valve control on the pumping line. Rastering of the targets was performed, along with scanning of the laser beam across the surface of the targets to improve thickness uniformity of the films.

Samples were heated from room temperature to the deposition temperature of 780°C at $\sim 1270°\mathrm{C/h}$. After deposition, the vacuum pumps and $\mathrm{O_2}$ pressure control were shut off and the films were cooled from 780°C to 500°C while increasing the $\mathrm{O_2}$ pressure to 1 Atm. The temperature was then held at 500°C for 30 minutes. The films were then cooled to room temperature. The (Y,Tb)123 layer thickness was initially estimated by comparing previous deposition runs in the chamber using the same deposition parameters.

The superconducting transition temperature $(\mathrm{T_c})$ and magnetic $\mathrm{J_c}$ measurements were made with a Quantum Design Model 6000 Physical Property Measurement System (PPMS) with a vibrating sample magnetometer (VSM) attachment. The $\mathrm{T_c}$s of the films were determined using a DC magnetization technique. The samples were mounted onto the end of a G-10 fiberglass rod and the magnetic moment of the material was measured as the samples were warmed from 60 K to 100 K at ~0.5 K/min. The magnitude of the applied field was 0.0025 T. The $\mathrm{T_c}$ measurements were precise to within 0.1 K.

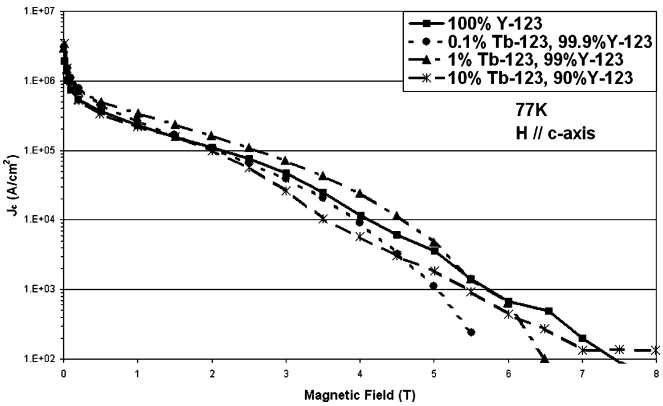

Fig. 1. Magnetic field dependence of $\mathrm{J_c}$ for Tb doped Y123 films at 77 K.

The magnetic $\mathrm{J_c}$ measurements was determined by subjecting the films to applied fields that varied from 0 to 9 T, with a ramp rate of 0.01 T/s. The $\mathrm{J_c}$ of the square samples was estimated using a simplified Bean model with $\mathrm{J_c} = 30\ \Delta \mathrm{M}/da^3$ where $\Delta \mathrm{M}$ is in emu, film thickness d and lateral dimension a are in cm and J is in $\mathrm{A/cm^2}$ [16]. Samples were subsequently acid-etched at the corners for thickness measurements. A KLA Tencor P-15 Profilometer was used to measure the thickness of the (Y,Tb)123 and (Y,Ce)123 films. Care was used to measure in twin-free areas of the LAO substrates, which were observed visually at high magnification. The film thickness and dimensions of each sample were measured multiple times to reduce errors in determination of the superconducting volume and a to $<5\%$.

III. RESULTS AND DISCUSSION

The $\mathrm{T_c}$s of the films as measured by DC magnetization are shown in Table I. As can be seen in the table, the $\mathrm{T_c}$s of Tb doped films (between 88.0 K and 89.5 K) are comparable to the Tc of reference Y123 films (89.2 K). However, the Ce doped films showed a marked decrease in $\mathrm{T_c}$ as the concentration of Ce increased, reaching a low value of 84.8 K. This is likely due to the Ce preferring to exist in a tetravalent state.

The magnetic $\mathrm{J_c}$s of the Tb and Ce doped films are also given in Table I. The graphs showing the magnetic field dependence of $\mathrm{J_c}$ for the films are in Figs. 1–4. Figs. 1 and 2 show magnetic field dependence of $\mathrm{J_c}$ at 77 K for Tb and Ce doped samples respectively. Figs. 3 and 4 show magnetic field dependence of $\mathrm{J_c}$ at 65 K for Tb and Ce doped Y123 respectively. At 0.01 T, the $\mathrm{J_c}$s of the Tb doped samples were all above 1 $\mathrm{MA/cm^2}$ while the

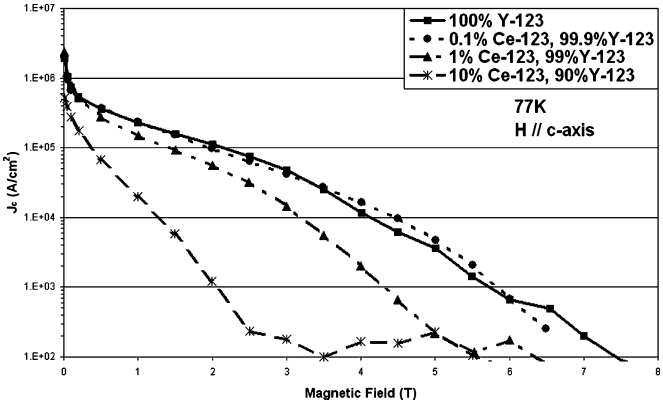

Fig. 2. Magnetic field dependence of J_c for Ce doped Y123 films at 77 K.

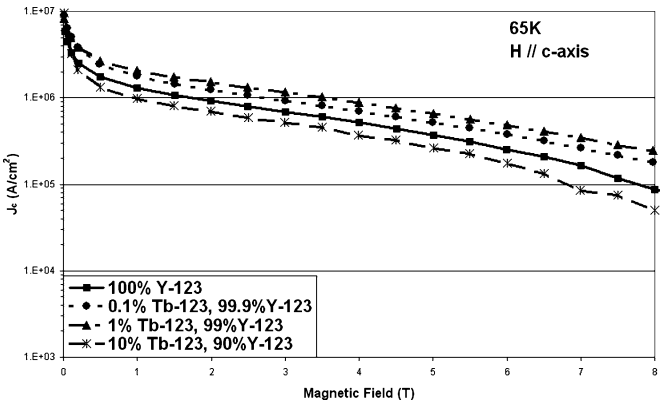

Fig. 3. Magnetic field dependence of J_c for Tb doped Y123 films at 65 K.

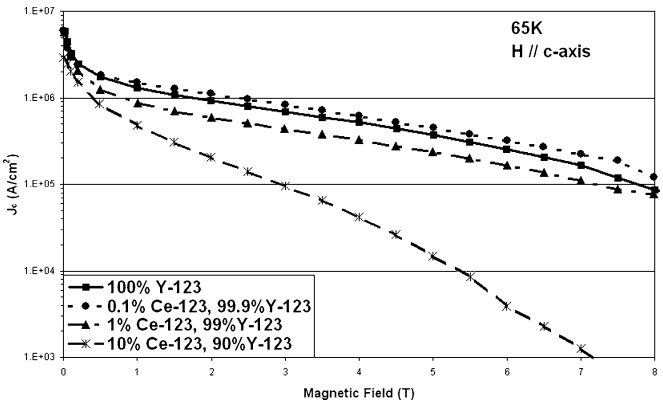

Fig. 4. Magnetic field dependence of Ce for J_c doped Y123 films at 65 K.

Ce samples J_cs decreased with increasing concentration of Ce from $1.65\,\mathrm{MA/cm^2}$ for $(Y_{0.999}Ce_{0.001})123$ to $\sim 0.5\,\mathrm{MA/cm^2}$ for $(Y_{0.90}Ce_{0.10})123$.

The most important feature of these results is that, at higher concentrations of 10% or greater (typically used for rare earth substitutions in Y123), these elements are detrimental to the in-field current density of YBCO, this is especially true in the case of Ce addition. This is constant with prior work indicating the degrading nature of these elements as inclusions into the Y123 structure [10]. However, when concentrations are reduced to smaller proportions, enhancement of J_c is possible. At 65 K, this is particularly apparent with 0.1% and 1% Tb and 0.1% Ce additions. The difference between the 1% Tb concentration and the 1% Ce concentration can be ascribed to the degrading effects of Ce on T_c, per previous work, whereas Tb does not produce such reductions in T_c. Perhaps the greater difficulty of this process for introducing pinning is obtaining a well dispersed mixture of $<0.1\%$ Tb or Ce. If possible, it is projected that better pinning properties can be realized, especially with Ce.

IV. Conclusions

Tb and Ce doped Y123 films were processed by PLD. Results suggest that doping Y123 with Tb produces films of good quality with similar properties to that of Y123. Decreasing the quantity of Tb to 1% or less appears to produce enhanced pinning characteristics of the resulting films especially at higher fields. However, the addition of Ce to Y123 films produces films of increasingly poorer quality as the concentration of Ce is increased in the films. However, it does appear that very minute additions of Ce ($\sim$0.1% Ce123 in Y123) may actually produce some favorable pinning characteristics to the films at high fields at 65 K.

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