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Published in: IEEE Transactions on Applied Superconductivity

Link to article, DOI: 10.1109/TASC.2016.2549558

Publication date: 2016

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Opata, Y. A., Wulff, A. C., Hansen, J. O. B., Yue, Z., & Grivel, J-C. (2016). Superconducting Dy$_{1-x}$(Gd,Yb)$_x$Ba$_2$Cu$_3$O$_{7-δ}$ thin films made by Chemical Solution Deposition. IEEE Transactions on Applied Superconductivity, 26(3), [7500705]. https://doi.org/10.1109/TASC.2016.2549558

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Superconducting $\text{Dy}_{1-x} \text{(Gd,Yb)}_x \text{Ba}_2 \text{Cu}_3 \text{O}_{7-\delta}$ thin films made by Chemical Solution Deposition

Yuri A. Opata, Anders C. Wulff, Jørn B. Hansen, Zhao Yue and Jean-Claude Grivel

Abstract—$\text{Dy}_{1-x} \text{(Gd or Yb)}_x \text{Ba}_2 \text{Cu}_3 \text{O}_{7-\delta}$ samples were prepared using chemical solution deposition (CSD), based on trifluoroacetate metal-organic decomposition (MOD) methods. X-ray diffraction results demonstrated the formation of the RE123 superconducting phase with a strong in-plane and out-of-plane texture. c-lattice constants were observed to decrease for all samples doped with Gd or Yb. Measurements of the onset critical transition temperature ($T_{\text{onset}}$) were found to decrease with increasing Yb content, while only minor changes were observed for samples with Gd. Critical current density ($J_c$) analysis demonstrated that doping with Yb significantly increased the self-field $J_c$ value from 3.8 MA/cm$^2$ to 6.0 MA/cm$^2$ for the pure and 10 % Yb doped sample, respectively. In contrast, samples doped with Gd were characterized by the lowest self-field $J_c$ values. Investigation of pinning force mechanisms revealed that the samples in this study were dominated by normal surface pinning.

Index Terms—Superconducting, thin film, pinning force, doping, critical current density.

I. INTRODUCTION

CHEMICAL solution deposition (CSD), based on trifluoroacetate metal-organic decomposition (MOD), is considered one of the most cost effective and scalable solutions for industrial production of long length and uniform superconducting coated conductors (CCs) with a high critical current ($I_c$) [1]–[4]. The latter is achieved by epitaxially growing a thin superconducting rare-earth-$\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE123) film on a strongly textured template. Improving the performance of the CC can be achieved by increasing $I_c$ either by producing thicker RE123 layers or increasing the critical current density $J_c$. Increasing the film thickness using CSD-MOD has proved difficult [2] compared to other deposition techniques [5], [6], while introducing artificial pinning centers by doping the RE123 has been demonstrated to significantly improve the magnetic-field $J_c$. Doping is typically performed either by RE [7]–[9] or Cu [10]–[12] substitution, or by adding elements, such as Zr or Y, to form non-superconducting nanoparticles [13]. Most work on increasing $J_c$ of RE123 films has been focused on RE-substitutions and doping with nanoparticles in YBa$_2$Cu$_3$O$_{7-\delta}$ (Y123) [14], [15] and GdBa$_2$Cu$_3$O$_{7-\delta}$ (Gd123) [16]. Such investigations in DyBa$_2$Cu$_3$O$_{7-\delta}$ (Dy123) have mainly been conducted on thin films made by inclined substrate deposition (ISD), thermal evaporation and molecular beam epitaxy [17]–[20]. The present work will focus on the changes in the structural and pinning properties of CSD-based $\text{Dy}_{1-x} \text{(Gd,Yb)}_x \text{Ba}_2 \text{Cu}_3 \text{O}_{7-\delta}$ thin films resulting from partial substitution of Dy$^{3+}$ by Gd$^{3+}$ and Yb$^{3+}$ ions.

II. EXPERIMENTAL PROCEDURE

$\text{Dy}_{1-x} \text{Gd}_x \text{Ba}_2 \text{Cu}_3 \text{O}_{7-\delta}$ (DyGd) and $\text{Dy}_{1-x} \text{Yb}_x \text{Ba}_2 \text{Cu}_3 \text{O}_{7-\delta}$ (DyYb), with $x = 0$, 0.1 and 0.2, thin films were synthesized by a metal-organic decomposition route [21]. The solutions were prepared as follows. Firstly, stoichiometric amounts of dysprosium, gadolinium and ytterbium acetate tetrahydrate and barium acetate were dissolved in trifluoroacetic anhydride and deionized water and stirred for 2 hours at 50 °C. Secondly, copper acetate monohydrate was dissolved in acetic acid and deionized water and stirred for 1 hour at 80 °C. After reaction the copper solution was dried by vacuum evaporation resulting in a viscous blue liquid. This process was also used to dry the dysprosium, gadolinium, ytterbium and barium solutions. The copper solution was then dissolved in methanol (99%) and mixed with the dysprosium (gadolinium, ytterbium)-barium solution and drying using vacuum evaporation. The final solution volume was adjusted to 1.5 M by adding methanol (99.9%). The precursor solutions were deposited on LaAlO$_3$ (LAO) single crystalline substrates at room temperature by spin-coating at 5000 rpm. Pyrolysis was performed by heating the sample in a furnace from room temperature to 180°C at 5°C/min, followed by a ramp to 350°C at 2.1°C/min and then to 400°C at 2°C/min. The furnace was kept at this temperature for 10 minutes, followed by cooling to room temperature. A humid oxygen flow was switched on at 100°C and kept until 400°C, ending the process with dry oxygen. After the pyrolysis, the films were subjected to a crystallization and sintering process, where the temperature was increased from room temperature to 720°C at 28°C/min, followed by heating with 18°C/min to 810°C. The latter temperature was kept for 135 min, ending with furnace cooling to room temperature. In this process, humid argon with 300 ppm of O$_2$ gas was used, switched on at 400°C and kept on until 30 minutes before the end of the process. During the last period the gas was dry in order to sinter the composites. Finally, oxygenation was carried out at 450°C for 3 hours in an oxygen flow.

Phase and crystallographic textures were analysed by X-ray diffraction (XRD) using Cu K$_\alpha$ radiation source, in a Rigaku four-circle diffractometer. Scanning electron microscopy images were acquired (SEM, Supra 35) to analyze the surface...
morphology with an in-lens detector. Magnetic properties were characterized in a vibrating sample magnetometer (VSM), where the superconducting transition temperature was determined using an AC susceptibility technique with an applied magnetic field amplitude of 0.1 mT and a frequency of 17 Hz. $J_c$ values were calculated using the Bean model. Analysis of the pinning force was also carried out [22].

### III. Results and Discussion

XRD patterns of all samples are presented in Fig. 1, where the (00l) reflections from the RE123 superconducting phase are indicated. These results show that RE123 phase formation was achieved, with strong c-axis orientation. Additionally, significant peaks from the single crystal substrate (LAO), and some minor reflections, due to RE123 (103) and (200) (see inset in Fig. 1) and Dy$_2$O$_3$ (400) were observed for all films. From the (00l) RE123 peaks positions, the c-axis lattice constant was calculated with the Nelson-Riley method [23]. The results are shown Fig. 2, as a function of the average ionic radius of the rare-earth nominal composition Dy$_{1-x}$(Gd,Yb)$_x$. For the Yb-doped films it is noticed that the c-axis value is reduced with the increase of the doping level, which can be ascribed to the smaller ion radius of Yb$^{3+}$ (0.985 Å) as compared to Dy$^{3+}$ (1.027 Å) [24]. In case of Gd-doped films, a reduction in c-axis is first observed ($c \approx 11.6855$), followed by an increase ($c \approx 11.6889$). An increase of the c lattice parameter would be expected, as observed in related doping studies [8], [25], because Gd$^{3+}$ has an ion radius (1.057 Å) larger than Dy$^{3+}$. This could be due to a partial replacement of Gd ions on Ba sites instead of Dy [26], [27], whereas there is not possibility for such ion exchange between Dy and Ba [28], [29].

![Figure 1](image1.png)

**Figure 1.** XRD diffraction patterns for all samples, where the peaks from films, substrate and other minor reflections are indexed. The inset shows a zoom of the region between 45°-49°, which shows the variation of the RE123 (200) peak.

![Figure 2](image2.png)

**Figure 2.** c-lattice constant - calculated from the Nelson-Riley method - as a function of the average ionic radius of nominal composition Dy$_{1-x}$(Gd,Yb)$_x$.

**Table I**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta \phi$ FWHM</th>
<th>$\Delta \omega$ FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy123</td>
<td>0.51°</td>
<td>0.39°</td>
</tr>
<tr>
<td>(Dy$<em>{0.9}$Gd$</em>{0.1}$)$_{123}$ - (DyGd10)</td>
<td>1.5°</td>
<td>0.74°</td>
</tr>
<tr>
<td>(Dy$<em>{0.9}$Gd$</em>{0.2}$)$_{123}$ - (DyGd20)</td>
<td>1.62°</td>
<td>0.58°</td>
</tr>
<tr>
<td>(Dy$<em>{0.9}$Yb$</em>{0.1}$)$_{123}$ - (DyYb10)</td>
<td>0.54°</td>
<td>0.26°</td>
</tr>
<tr>
<td>(Dy$<em>{0.8}$Yb$</em>{0.2}$)$_{123}$ - (DyYb20)</td>
<td>1.32°</td>
<td>0.3°</td>
</tr>
</tbody>
</table>

Fig. 3 a-e shows the surface morphology for the DyBa$_2$Cu$_3$O$_{7-\delta}$ and (Gd,Yb)-doped films. A crack-free and dense surface is observed for all films. Some a/b-axis oriented grains (white solid ellipse) are observed, as confirmed also by the XRD data. It is found that the particles (white dashed circles) and the fraction of pores are reduced with the increasing of doping level, except in the DyYb10 case, where an increase in the particles is observed. The reason behind the modification of the density of the pores is not clear, but it might be related to the difference in peritectic melting values, being 1020°C, 1010°C and 950°C to Gd123, Dy123 and Yb123 respectively [30]. Film thickness analysis was performed by SEM cross-section observation after mechanically breaking the films, as shown in Fig. 3f for the DyGd20 sample. The average thickness was calculated using the values measured along the entire length of each film. An average value of 320 nm was found for the films, except of the DyYb10 sample, which exhibits a value around 270 nm.

The texture quality of the samples was investigated by (103) phi-scans and (005) rocking curves. Details of the texture analysis are presented in Table I. The full width at half maximum values (FWHM) demonstrate that a good in-plane ($\Delta \phi$) and out-of-plane ($\Delta \omega$) alignment is present in all films. An increase of the $\Delta \phi$ values are observed for doping with Yb and Gd, indicates a degradation of the in-plane texture due to lattice deformation caused by the doping [7].

![Image 49x141 to 306x335](image4.png)

**Figure 3**

Details of Texture Analysis for all thin films.
Figure 3. SEM images of the thin films: (a) Dy123; (b) DyGd10; (c) DyGd20; (d) DyYb10 and (e) DyYb20. (f) shows the cross section of sample DyGd20. White dashed circles indicate some particles while white solid ellipses highlight some a/b-axis oriented grains.

value is slightly lowered by Yb-doping, in contrast to Gad-doping which seems to have a lower effect on $T_{\text{onset}}^c$ value.

Figure 4. AC susceptibility curves for all investigated films. The inset shows the $T_{\text{onset}}^c$ values as a function of x doping level.

The $J_c$ values, as a function of applied magnetic field for all thin films are shown in Fig. 5. The highest critical current density self-field ($J_{c}^{sf}$) - see inset in Fig. 5 - were observed for the Yb-doped films, with the maximum of 6.0 MA/cm$^2$ in the DyYb10 sample. In contrast, the Gd-doped films exhibit lower values, with $J_{c}^{sf} = 2.61$ MA/cm$^2$ for DyGd20. Three different regimes are observed: a plateau at low magnetic field, associated to single-pinning regime, followed by a power-law $J_c(B) \sim B^{-\alpha}$ behaviour (see $\alpha$ values in Fig. 5), assigned to vortices collective interaction, which precedes the rapid decrease of $J_c$, as a result of flux creep [21]. Flux pinning force ($F_p = J_c \times B$) results are shown in Fig. 6, where the Yb-doped and pure films exhibit the highest maximum pinning force ($F_p^{max}$) values at 77 K, whereas the Gd-doped films show lower values. It is suggested that such result could be due to partial substitution of Gd on the Ba sites, causing a decrease in both $J_c^{sf}$ and $F_p$. On the other hand, the higher $J_c^{sf}$ values observed in DyYb10 film can be assigned to a strong texture ($\Delta \omega$) observed in this sample, as reported in Table I. This is supported by the low (103) and (200) peaks in Fig. 1. Another possible contribution to the improved $J_c$ is the lower amount of porosity in the Y-doped films, while the large difference in ion size between Dy and Yb (0.042 Å) compared to Dy versus Gd (0.026 Å) can also have a positive effect [8], [14].

Figure 5. Double logarithmic plot of the critical current density against applied magnetic field at 77K, for all films. The inset table summarizes the $J_{c}^{sf}$ and $\alpha$ values of the power-law dependence $J_c(B) \sim B^{-\alpha}$.
To analyse the flux pinning mechanism, we applied a modified Kramer and Dew-Hughes model [22], where the curve of \( f = F_p/F^\text{Max}_p \) vs \( h = B/B^* \) is fitted according to equation

\[
 f = \sum_{i=1}^{6} a_i h^{p_i} (1 - h)^{q_i} \tag{1}
\]

The \( B^* \) values were determined by plotting \( J_c^{1/2} B^{1/4} \) vs \( B \) [31], [32]. The parameters \( p_i \) and \( q_i \) are associated to different kinds of pinning mechanisms depending on their values [33], as listed below:

- \( p_1 = 0, q_1 = 2 \): normal, volume pinning (\( V_N \));
- \( p_2 = 1, q_2 = 1 \): \( \Delta \kappa \), volume pinning (\( V_\kappa \));
- \( p_3 = 1/2, q_3 = 2 \): normal, surface pinning (\( S_N \));
- \( p_4 = 3/2, q_4 = 1 \): \( \Delta \kappa \), surface pinning (\( S_\kappa \));
- \( p_5 = 1, q_5 = 2 \): normal, point pinning (\( P_N \));
- \( p_6 = 2, q_6 = 1 \): \( \Delta \kappa \), point pinning (\( P_\kappa \)).

The \( a_i \) constants represent the weight of each kind of pinning mechanism and \( a_j(\%) = 100 \times \sum_{i=1}^{6} (a_j/a_i) \) represent the percentage contribution of each pinning mechanism, reported as \( V_{N,k} \), \( S_{N,k} \), or \( P_{N,k} \). The fitted results for the different flux pinning mechanisms are listed in Table II, together with the \( B^* \) and \( h \) (at \( F^\text{Max}_p \) position) values. These results indicate that the pinning mechanism is dominated by normal surface pinning (\( S_N \)), in agreement with [7], [11], [34] who attributed this effect to be a result of dislocations. In this work, it is observed that the \( S_N \) values are lower than compared to the un-doped Dy123 sample for the investigated range of doping levels (10-20%). This indicates that the details of the the flux pinning mechanism are affected by doping, however the main pinning mechanism remain the same, whereas subtle variations cannot be inferred with certainty due to the large number of fitting parameters included in the model. Some differences in pinning could be assigned to the presence of nanoparticles, as for example RE\(_2\)O\(_3\) or inclusions of Cu-rich phases [34], or also slight variations in the texture of the sample.

### Table II

<table>
<thead>
<tr>
<th></th>
<th>Dy123</th>
<th>DyGd10</th>
<th>DyGd20</th>
<th>DyYb10</th>
<th>DyYb20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B^* ) (T)</td>
<td>6.12</td>
<td>5.93</td>
<td>6.78</td>
<td>5.50</td>
<td>6.29</td>
</tr>
<tr>
<td>( h ) at ( F^\text{Max}_p )</td>
<td>0.16</td>
<td>0.19</td>
<td>0.13</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>( V_N(%) )</td>
<td>6</td>
<td>7</td>
<td>11</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>( V_\kappa(%) )</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>( S_N(%) )</td>
<td>94</td>
<td>75</td>
<td>86</td>
<td>77</td>
<td>81</td>
</tr>
<tr>
<td>( S_\kappa(%) )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>( P_N(%) )</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>( P_\kappa(%) )</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

In this work, we investigated the changes in structural properties and variations in the magnetic flux pinning mechanism caused by the substitution of Gd and Yb ions (10-20%) in superconducting Dy\(_{1-x}\)(Gd,Yb)\(_2\)Ba\(_2\)Cu\(_3\)O\(_{7-\delta}\) thin films, prepared by trifluoroacetate metal-organic decomposition methods. XRD \( \theta-2\theta \) line profile analysis demonstrated that the samples exhibited the 123-phase. Strong in-plane and out-of-plane textures were observed for all the thin films, with the lowest full-width-at-half-maximum values obtained for the Dy\(_{0.9}\)Yb\(_{0.1}\)Ba\(_2\)Cu\(_3\)O\(_{7-\delta}\) sample. From a comparison of the c-lattice constants (\( c \)) it is evident that this parameter decreases upon doping with 10-20 % Yb or Gd in the DyBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) thin films. Using vibrating sample magnetometer analysis it was proved that doping with Yb, in this range, significantly decreased the onset critical temperature, while this value was nearly unaffected upon doping with Gd. In contrast, the critical current density values (\( J_c \)) at self-field, for the samples with Yb-doping were larger than the un-doped one, with the maximum \( J_c(77K) = 6.0 \text{ MA/cm}^2 \) (self-field) for the sample with 10% Yb. Compared to the un-doped film, both Gd-doped samples showed lower \( J_c \) values in self-field. Flux pinning force analysis showed that also the highest pinning force was observed in the samples with Yb (more than 1.9 GN/m\(^3\)), while the lowest pinning force value was observed for the sample with 10% Gd (1.55 GN/m\(^3\)). Finally, a flux pinning model was applied to the pinning force curves and it was found that normal surface pinning was the dominating pinning mechanism in all the films, with only minor contributions from point pinning detected for the samples with 10% doping.

REFERENCES


