Single and Binary Rare Earth $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Films Prepared by Chemical Solution Deposition

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Abstract: In the present work, a series of single and binary rare earth $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (REBCO, RE=Y, Ho etc.) thin films, such as YBCO, HoBCO and $\text{Y}_{0.7}\text{Ho}_{0.3}\text{BCO}$, were prepared by TFA-MOD process. Screw-growth mode and island-like surface were clearly observed in the present samples. Good c-axis orientation and high in-plane texture were identified in the all studied samples by measuring four circle X-ray diffractions (XRD). Theta-2Theta patterns of XRD showed no extra phases other than REBCO. As for HoBCO and $\text{Y}_{0.7}\text{Ho}_{0.3}\text{BCO}$ thin films, the temperature dependences of resistance were investigated in various applied magnetic fields (< 9T). Irreversibility fields ($H_{irr}$), characterised with a criteria of zero resistance in R-T curves, showed a similar superconducting behavior between single and binary REBCO, i.e. no obvious changes in performance due to Ho doping in YBCO.

1. Introduction

Second generation high temperature superconducting wires (2G) based on the REBCO coated conductor have been under development world-wide and is on the way to commercial application [1-3]. Among various approaches making superconductive layer, the Chemical Solution Deposition (CSD) that uses trifluoroacetate (TFA-MOD) is considered to be a low-cost process producing high $J_c$ values films [4-6]. The TFA-MOD process enables us to fabricate YBCO films with high critical current density ($J_c$) values over 3MA/cm$^2$ at 77K on both single crystal substrates and metallic tapes. In particular, the RABiTS/MOD technical approach provides an excellent path to the low cost manufacturing of 2G HTS wires.

In the REBCO superconductor, yttrium can be replaced by most of the other rare earth elements (except for Ce, Pr and Tb) without changing the structural framework or affecting the superconductivity. It is reported that the HoBCO thin films prepared by PLD indicate better durability than YBCO film in the ambient of high humidity [7]. The deposition rate of HoBCO is approximately two to three times faster than that of YBCO. And in high magnetic field, the critical current density of HoBCO is higher than YBCO [8].

It is reported that critical current density ($J_c$) values and flux pinning can be improved by adding elements to YBCO samples [9, 10]. In particular, it is worthwhile noticing that RE doping can result in a significant enhancement of $J_c$ for Y-123 superconductors [11, 12]. In TFA-MOD process, RE doping can be easily incorporated into the MOD process. Because the composition of the films can be easily changed through chemical modification of the MOD precursor solution.
In the present work, a series of single and binary rare earth $\text{REBa}_2\text{Cu}_3\text{O}_7-\delta$ ($\text{REBCO, } \text{RE}=\text{Y, Ho etc.}$) thin films, such as YBCO, HoBCO and $\text{Y}_{0.7}\text{Ho}_{0.3}\text{BCO}$, are prepared by TFA-MOD technique. By studying the crystalline orientation, AC susceptibility, critical current density, magneto-resistance properties, morphology and surface quality, we attempt to understand the crystal growth mechanism and superconducting properties of the $\text{REBCO}$ films in TFA-MOD process.

2. Experimental
The precursor solutions are prepared by reacting the acetates of yttrium (holmium), barium, and copper in the $1:2:3$ cation ratio and trifluoroacetic acid in deionized water, drying the product to a semisolid state, redissolving the product in methanol. At last, the residue is dissolved in sufficient methanol to get the trifluoroacetate precursor solution, whose concentration is $1.5\text{mol/L}$ [13, 14]. The HoBCO solution is mixed with the YBCO solution at the ratio of 7:3 to get the final mixed solution. All solutions are deposited on [100] oriented LaAlO$_3$ (LAO) single crystalline substrates. The gel films are treated through two heating steps to fabricate superconducting films. In this process, the films are heated to the maximum temperature ($T_{\text{max}}$) of $800^\circ\text{C}$. The partial pressure of oxygen ($P_{\text{O}_2}$) of the mixture gas is 0.1%. $P_{(\text{H}_2\text{O})}$ of the humid gas is about 4.2%.

The preferred orientations and the texture of the prepared samples are investigated using x-ray diffraction. The morphology and surface quality is investigated by Atom Force Microscope (AFM). AC susceptibility measurements are performed using inductive devices. Critical current density is evaluated by inductive technique as well. Resistivity measurements and magnetotransport measurements using a standard four-contact method are measured at various temperatures and magnetic fields using a Quantum Design PPMS. Magnetic field is applied parallel to the $c$ axis.

3. Results and Discussion
3.1. Texture analysis and Surface morphology
Figure 1 shows the XRD patterns of the YBCO, HoBCO and $\text{Y}_{0.7}\text{Ho}_{0.3}\text{BCO}$ prepared by TFA-MOD.

Figure 1. XRD patterns of the YBCO, HoBCO and $\text{Y}_{0.7}\text{Ho}_{0.3}\text{BCO}$ prepared by TFA-MOD

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spots. It is seen that the FWHM value of the in-plane orientation of the sample $Y_{0.7}H_{0.3}BCO$ is $0.8^\circ$, indicating the excellent out-plane and in-plane grain alignment. The FWHM values are similar between the single $REBCO$ layer and binary films, suggesting that the texture quality is not reduced by Ho doping.

![Figure 2. Pole figure (a) and phi scan (b) of (103) $Y_{0.7}H_{0.3}BCO$.](image)

A typical AFM image for MOD-HoBCO is shown in Figure 3. Screw-growth mode and island-like surface are clearly observed in all present samples. Average island size is in the range of 300nm. In general, the surface is rather flat and smooth, with the RMS of 27 nm. We can see no big difference in surface morphology between HoBCO and YBCO thin films.

![Figure 3. Growth island characteristics under AFM observation of HoBCO film.](image)

3.2. Superconducting properties
Critical superconducting temperature $T_c$ of all the films is around 90 K, with a transition width of 1.0k. Figure 4 shows the temperature dependencies of the normalized real and imaginary parts of AC susceptibility for different frequency at voltage amplitude voltage of 3V. It is suggested that
YBCO and HoBCO have a similar flux pinning characterization, as they have a similar peak shifting behavior. It is also confirmed by measuring inductive \( J_c \). The measurement of inductive \( J_c \) at zero field and 77K reveals a value of 2.63 MA/cm² for HoBCO, in contrast with 2.53MA/cm² for YBCO.

To confirm the similar superconducting properties, magnetotransport measurements of HoBCO and \( Y_{0.7}Ho_{0.3}BCO \) films are measured in various magnetic fields. Both have the similar Irreversibility line (characterised with a criteria of zero resistance in R-T curves), as shown in Fig. 5. In Ho-doped YBCO superconducting films, it is found that Ho doping does not influence the superconducting properties. These are different from the case of ternary rare earth mixed (Nd, Eu, Gd) BCO [15] where a strong flux pinning improvement is emerged due to stress fields arising from the lattice mismatch. Possible reasons may be related to the following factors: Firstly, Y sites are not substituted by Ho based on the nominal composition in the present processing conditions; Secondly, the radius of Ho\(^{3+}\) (1.05Å) is close to that of Y\(^{3+}\) (1.06Å), unlike the pronounceable lattice mismatch among Nd, Eu, and Gd. Due to their close lattice parameters, the influence created by the partial substitution of Ho for Y is small.

**Figure 4.** Temperature dependence of normalized imaginary (a) and real (b) parts of AC susceptibility

**Figure 5.** Magnetotransport comparison between HoBCO and \( Y_{0.7}Ho_{0.3}BCO \) films: (a)Resistance vs. temperature in various magnetic field; (b) Irreversibility fields vs. reduced temperatures
4. Summary
We have obtained high quality YBCO, HoBCO and Y0.7Ho0.3BCO films on (100) LaAlO3 by TFA-MOD process. All the films are c-axis oriented and show a critical superconducting temperature $T_c$ of about 90k. Moreover, the three types of films have similar superconducting properties, which suggesting that element substitutions between Ho and Y does not lead to pronounced improvement on flux pinning due to their close lattice parameters and possible low exchange ratio in the present processing condition.

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