Preparation of YBCO-BYTO and YBCO-BZO nanostructured superconducting films by chemical method

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Abstract. YBCO-BYTO6% and YBCO-BZO10% $YBa_2Cu_3O_{7-d}$-Ba_2YTaO_6 6% (YBCO-BYTO6%) and $YBa_2Cu_3O_7$-$BaZrO_3$ 10% (YBCO-BZO 10%) nanostructured films were grown by the Chemical Solution Deposition method, and compared with YBCO pure films. Films were deposited on YSZ substrates, with $Ce_{0.9}Zr_{0.1}O_2$ and $Ce_{0.6}Zr_{0.4}O_2$ buffer layers. They were characterized by GADDS X-ray diffraction, scanning electron microscopy (SEM) and inductive (SQUID) measurements of the critical temperature (T_c) and critical current density (J_c). It was found that YBCO-BZO10% films presented better superconducting properties (T_c=89.2K and J_c=1.3MA/cm^2), probably due to an enhanced pinning force, originated by BZO nanoparticles. Additionally, it was found that these films have lower reactivity with the buffer layer.

1. Introduction

The development of low-cost superconducting tapes requires the use of multilayer structures where the texture is preserved between the different layers, and reactivity between the superconducting film and substrate is minimized. Growth ex-situ techniques are subject of intense research in order to obtain coated conductors (CC), with YBCO, at low cost and with high critical current density. To make buffer layers with different architectures, some methods, like vacuum deposition (PLD and sputtering), or chemical solution deposition methods (CSD), including sol-gel and MOD, can be used. The production cost is higher in the case of vacuum deposition methods, while in CSD the equipment is simpler; therefore, the cost is very attractive. The main goal of optimizing the production cost to quality ratio is obtained in a CC where all layers are grown by chemical methods, known as full chemical route [1].

YBCO nanocomposite materials have opened new paths to achieve enhancement of vortex pinning, therefore increasing the critical current density, J_c. Fabrication of nanostructured YBCO thin films with incorporation of nanosized oxides as secondary non superconducting phases, has produced strong enhancement of YBCO performance at high magnetic fields, in a wide temperature range. These results boost the potential use of these materials in a broad spectrum of applications [2-5].
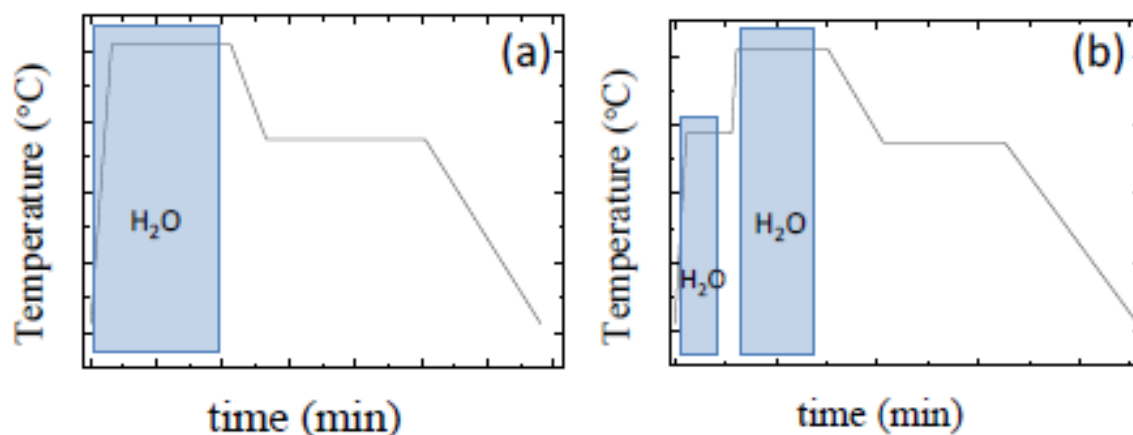
Cerium dioxide (CeO_2), has been widely used as buffer layer for growing HTS [6]. Several groups have attempted to use it for YBCO CC because of its excellent chemical compatibility with Ni substrates, as well as a good foundation for the growth of YBCO. Unfortunately, due to the existence of a critical thickness of 50nm, above which cracks and microcracks are formed, CeO_2 rarely has been used successfully. Alternatively, the use of CeO_2 doped with Zr^{4+}, $Ce_xZr_{1-X}O_2$ (CZO), allows the growth of atomically flat and free of cracks epitaxial layers. Such advantage has been attributed to reconstruction of grain boundaries, due to increased atomic mobility, that allows complete eradication of carbon atoms

in grain boundaries [7]. CSD is a cost-effective technique for preparation of large area and long length films [6]. Metallorganic decomposition (MOD) of trifluoroacetate (TFA) has been widely investigated as a chemical solution route leading to high quality YBCO nanocomposite films, with high J_c [8].

In this work a reference pure YBCO film was made, and nanostructured YBCO films, using secondary phases of BYTO6% (YBYTO) and BZO10% (YBZO), by the TFA route. They were deposited on ytrium stabilized zirconia (YSZ) substrates, with $Ce_{0.9}Zr_{0.1}O_2$ (CZO-0.1) and $Ce_{0.6}Zr_{0.4}O_2$ (CZO-0.4) buffer layers. Films were characterized by GADDS X-ray diffraction, SEM and inductive (SQUID) measurements for the determination of T_c and J_c.

2. Experimental details

YBCO films were prepared by the trifluoroacetates route by using anhydrous precursor solution with 1.5M concentration [9], as described in detail elsewhere [4]. The metallorganic precursor solution was spin coated on crystalline substrates of YSZ/CZO of $5\times5mm^2$. Then a thermal treatment for pyrolysis was made, under oxygen flow, at 300°C, for 30min [2]. The crystallization process was performed following the thermal cycle shown in Figure 1(a), in a wet N_2 atmosphere, with a water vapor partial pressure of 22 mbar, and O_2 partial pressure of 0.2 mbar. Finally, the superconducting phase was obtained by annealing at 450°C, in oxygen atmosphere. YBYTO and YBZO films were made by adding stoichiometric amounts of tantalum ethoxide and Zirconium acetylacetonate in a precursor TFA-YBCO solution, as described elsewhere [3,10,11]. The metallorganic precursor solution was spin coated on crystalline substrates of YSZ/CZO, $5\times5mm^2$. The pyrolysis process was to the same performed on samples of pure YBCO. The crystallization process was made following the thermal cycle shown in Figure 1(b). The superconducting phase was obtained by annealing at 450°C, in oxygen atmosphere.

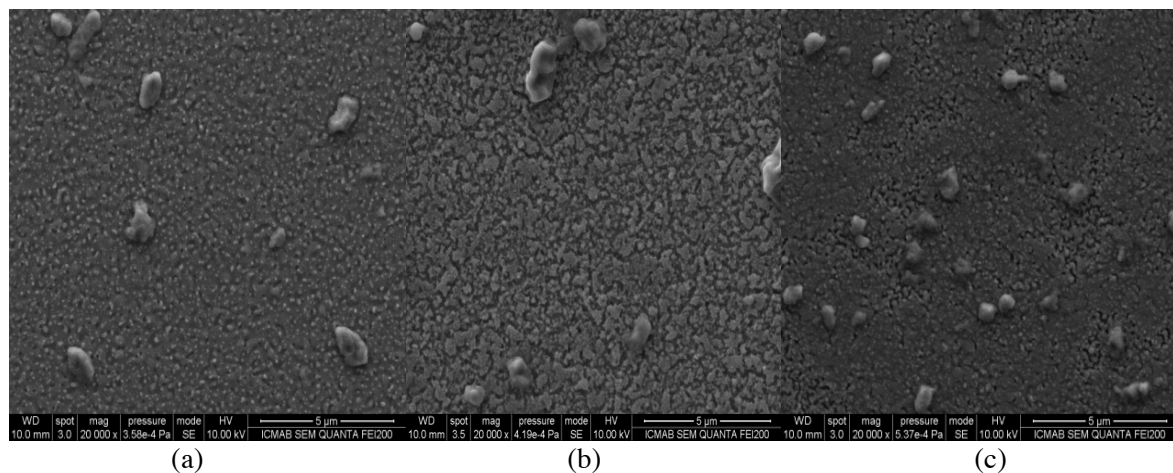**Figure 1**. Scheme of the thermal process used to prepare the films: (a) YBCO, (b) YBYTO and YBZO.

The microstructure and phase analysis of the films were studied by two-dimensional X-ray diffraction with a Bruker AXS GADDS diffractometer, and SEM microscopy with a FEI Quanta 200 FEG microscope. The critical current density (J_c) and critical temperature (T_c) were obtained inductively with a Quantum Design MPMS-XL SQUID magnetometer.
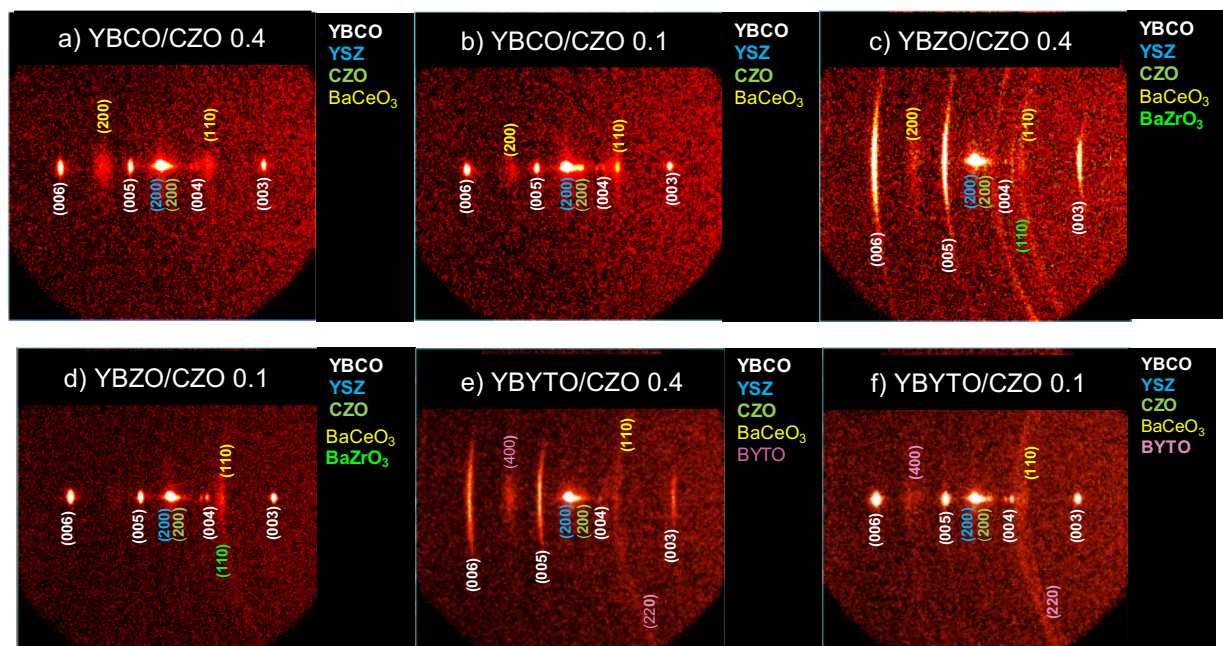
3. Results and discussion

In the SEM micrographs in Figure 2 can be observed the morphology of the samples grown on YSZ/CZO-0.1. In all of them there are some precipitate grains of $BaCuO_2$, as confirmed by EDX. There is lower porosity and a smoother surface in the sample YBZO, indicating a better quality film.

Figure 3 presents GADDS images of the samples. For pure YBCO films, deposited on the two kinds of substrates (Figures 3(a) and 3(b)), we do not observe a big difference between the two images. In the YBZO films, for the substrate CZO-0.4 (Figure 3(c)), reflections appear as spots and rings, indicating

coexistence of oriented and random YBCO. In contrast, for the substrate CZO-0.1 (Figure 3(d)) reflections are more spot like, indicating a much better crystalline orientation. Something similar happens with the YBYTO films, as shown in Figures 3(e) and 3(f). Thus it can be concluded that the best stoichiometry of the buffer layer for growing nanostructured films is CZO-0.1. From these figures we also conclude that among the two nanostructured films the best epitaxial growth is obtained in YBZO on CZO-0.1. This result agrees with the SEM images of Figure 2, and will be later supported by the superconducting properties. Furthermore, in Figure 3, we observe that reflections of nanoparticles: (220) of BYTO, and (110) of BZO, appear as rings, indicating they are mostly randomly oriented, which is a desirable characteristic [3,5].
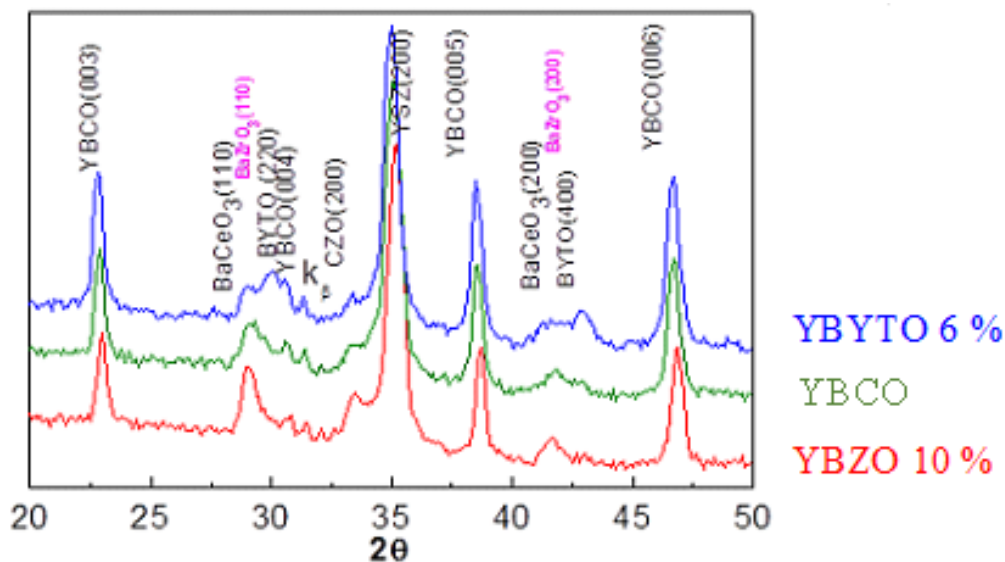

Figure 2. SEM micrographs of YBCO and nanostructured YBCO films grown on YSZ/CZO-0.1 substrates: (a) YBCO, (b) YBYTO and (c) YBZO. The best quality film, with lower porosity and smoother surface, is YBZO.

Figure 3. GADDS images for samples: (a) YBCO/CZO-0.4, (b) YBCO/CZO-0.1, (c) YBZO/CZO-0.4 d) YBZO/CZO-0.1, (d) YBYTO/CZO-0.4, (f) YBYTO/CZO-0.1. X-ray reflections are more spot like for films deposited don the CZO-0.1 substrates (right side images).

The conventional diffractogram presented in Figure 4 is obtained by integrating the above GADDS data, for the films deposited on CZO-0.1. This allows a better assessment of the intensity relation of the present phases. The diffractogram contains peaks of c-axis oriented YBCO, peaks of the buffer layer CZO, and peaks of the substrate YSZ, as indicated in the figure. In the YBYTO film there are peaks (220) and (400) of BYTO. In all samples there are peaks (110) and (220) of $BaCeO_3$, resulting from chemical reaction with the buffer layer, although in BYTO these peaks have lower intensity.

Figure 4. Diffractogram for YBCO, YBZO and YBYTO films grown on CZO-0.1. This graph is obtained by integration of the 2D GADDS information in Figure 3.
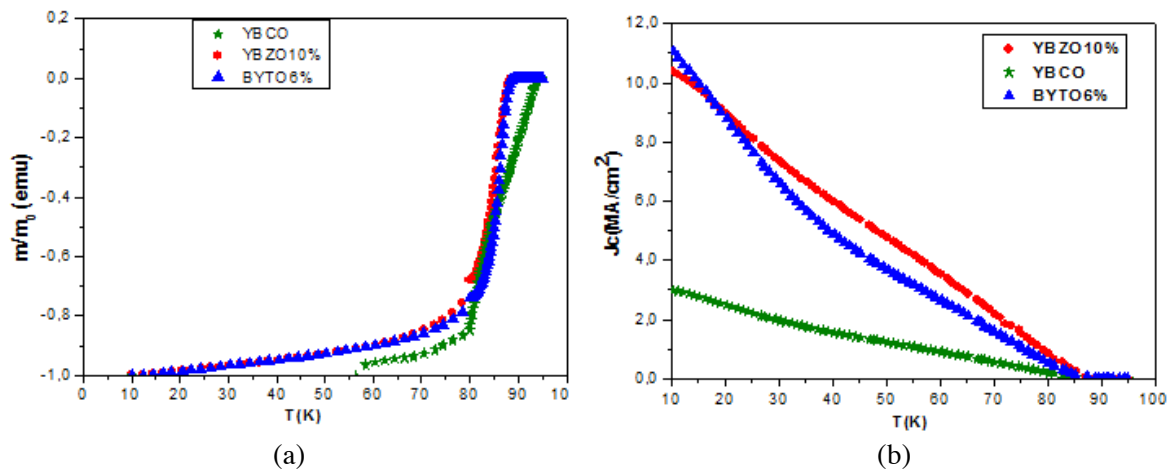
Figure 5 presents the inductive measurements of T_c and J_c, for the samples grown on CZO-0.1. Figure 5(a) shows the magnetization as function of temperature, from which we obtain T_c, which is practically the same ~89.5K, for all samples. The transition width, ΔT, in the films YBZO (8.2K) and YBYTO (8.0K), have lower values than pure YBCO (9.0K), indicating higher homogeneity in the nanostructured films. These results are summarized in Table 1. Figure 5(b) shows J_c, as function of temperature. The best behaviour is observed in sample YBZO, followed by YBYTO, with a clear increase of J_c over the pure YBCO sample. J_c was enhanced in YBZO by a factor of ~4, with respect to pure YBCO, over the whole temperature range. Table 1 presents values of J_c at 77K, for comparison. These results are compelling evidence of improvement of the superconducting properties in nanostructured films, compared with pure YBCO.

Table 1. Superconducting properties of the films grown on CZO-0.1/YSZ.

Sample	T_c(K)	ΔT (K)	J_c(77K)MA/cm^2
YBCO	90.0	9.0	0.3
YBYTO	89.5	8.0	1.0
YBZO	89.2	8.2	1.3

The higher J_c values obtained in nanostructured films is due to the pinning centres originated by the nanoparticles. In addition, in these films there is less reactivity with the buffer layer, according to XRD (Figure 4) and SEM (Figure 2) results.

(a)   (b)

Figure 5. Inductive measurements of T_c and J_c, for YBCO, YBZO and YBYTO films, grown on CZO-0.1. (a) Normalized magnetization, where T_c is obtained, and (b) J_c. The best sample, according to these superconducting properties, is YBZO.

4. Conclusions

Pure YBCO and nanostructured YBZO10% and YBYTO 6% films were grown on YSZ substrates with buffer layers of CZO-0.1 and CZO-0.4. The buffer layer CZO-0.1 produced better epitaxial growth of the deposited films, than CZO-0.4. Nanostructured films presented better morphology, epitaxial growth and superconducting properties than pure YBCO. The best sample in all respects was YBZO10%, where J_c was enhanced by a factor of ~4 over the corresponding value in pure YBCO, in the temperature range from 10K to 77K. This sample has T_c= 89.2K and J_c = 1.3MA/cm^2 at 10K. These results are quite promising for a sample made by a chemical method, encouraging further research in this direction. A next step in this research is to optimize the thermal process in order to reduce chemical reaction between the nanostructured film and the buffer layer.

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