

YBa₂Cu₃O₇-CeO₂ superconducting epitaxial thin films: Growth and structural characterization

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Abstract: YBa₂Cu₃O₇ 95%- CeO₂ 5% nanocomposite thin films on monocrystalline SrTiO₃(001) and LaAlO₃(001) substrates were obtained using Pulsed Laser Deposition technique. Their crystalline structure, morphology and electrical resistance versus temperature behavior were obtained and compared with conventional (single) YBa₂Cu₃O₇ thin films. The nanocomposite samples are c-axis oriented and epitaxial as conventional films, and remarkably have a significantly lower roughness than conventional YBCO samples. YBa₂Cu₃O₇-CeO₂ nanocomposite films maintain the superconducting character with high T_c around 88K and they have a narrow transition width of 2K.

I. INTRODUCTION

YBa₂Cu₃O₇(YBCO) is one of the most studied of high temperature superconductors. In order to improve the electrical properties (critical current and its dependence with temperature and magnetic fields), CeO₂ nanocrystals can be added to create some defects that can pin the vortex present in type II superconductors[1-2]. Thanks to the vortex pinning at the nanocrystals, J_c can be higher than it would be in conventional YBCO thin films. The objective of this study is based on de deposition and characterization of YBCO doped with 5% CeO₂ thin films on single crystalline substrates and on their comparison with standard (CeO₂ free) YBCO films. We focus here on structural properties and preliminary electrical measurements (R(T)), without investigation of the critical currents.

Thin films were deposited by Pulsed Laser Deposition (PLD). This technique is particularly useful to deposit complex oxides as YBCO, so it has been very common to grow YBCO films using this technique. Due to this fact, physical deposition parameters are already optimized to get high quality films. Two kinds of substrates have been used: SrTiO₃ (001) oriented (STO) and LaAlO₃ (001) oriented (LAO), because of the similarity on their lattice parameters with YBCO's. STO is cubic with lattice parameter a=3.905Å, LAO is close to cubic with a=3.863Å and YBCO is orthorhombic with a=3.823Å, b=3.887Å and c=11.680Å. The lattice matching between YBCO and the substrate is essential in obtaining good epitaxial films. Because of that, they are the most used substrates to grow this material[3].

The study of the properties of the films includes the characterization of its crystalline structure (analysis of the epitaxy of the films), their morphology and the measurement of the electrical resistance as a function of temperature. This properties are compared with those of YBCO films without CeO₂ doping.

II. EXPERIMENTAL

A. Growth of the samples

All samples were grown by Pulsed Laser Deposition using the equipment of the GECFE group of the UB. It's a Physical Vapour Deposition technique based on the

interaction of an intense UV laser beam with a bulk piece of the material (target) in a vacuum chamber. The laser beam is of short wavelength (284nm) and pulsed, and it is focused above a threshold energy density. These conditions cause the ablation of the target and the material is deposited on the substrate. Figure 1 shows the basics of a standard Pulsed Laser Deposition system. It's a powerful technique to deposit complex oxides because the complex stoichiometry of the materials is maintained[4-5].

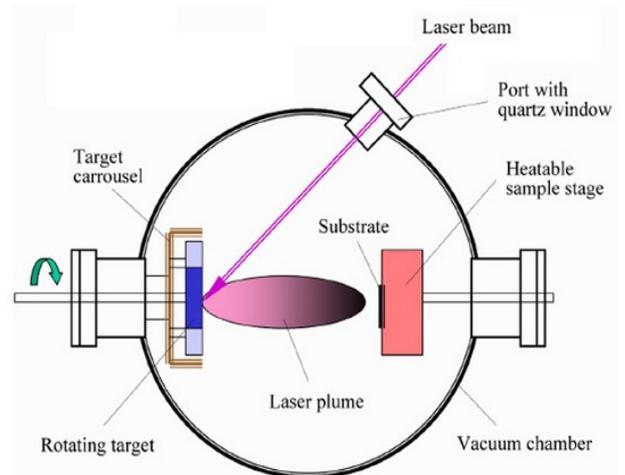


FIG. 1: Standard PLD chamber.

The most relevant deposition parameters that have to be taken in control due to their impact on the film properties are the substrate temperature and the partial pressure of O₂. The thickness of the sample can be directly controlled with the number of pulses. In this study, the O₂ pressure has been fixed at 0.3mbar and the substrate temperature is 800°C. The number of pulses has been a variable parameter on the grown samples.

The substrates used to grow YBCO and YBCO-CeO₂ are monocrystalline STO(100) and LAO(100) because the lattice parameter is quite similar to them and it eases the epitaxial growth.

The samples growth for this study and their growth characteristics are shown in TABLE I.

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Material	Substrate	Substrate temperature	pO ₂	Thickness
YBCO	STO	800°C	0.3mbar	80nm
YBCO	STO	800°C	0.3mbar	120nm
YBCO-CeO ₂	STO	800°C	0.3mbar	120nm
YBCO	LAO	800°C	0.3mbar	80nm
YBCO	LAO	800°C	0.3mbar	120nm
YBCO-CeO ₂	LAO	800°C	0.3mbar	120nm

TABLE I: Deposition parameters of the grown samples.

B. Characterization

The samples were characterised using three different techniques. Atomic Force Microscopy (AFM) was used to get information of the morphology: uniformity and roughness of the sample's surface. These measurements have been realised with the GECFE equipment of the University of Barcelona. In AFM, a tip scans the sample giving information about height differences. The data acquired of each point is collected in a map of heights of the surface.

The crystalline structure characterization has been done by X-Ray diffractometry (XRD) in the equipment of Centres Científics i Tecnològics de la Universitat de Barcelona (CciTUB). It is based on a X-Ray beam that interacts with the material. Due to its crystalline structure, the material diffracts the beam at certain angles directly related with the atomical positions. 2θ - ω (around symmetrical reflections) and Φ (around asymmetrical reflections) scans were measured. These scans allow us to get information about out of plane and in plane structure respectively.

The electrical resistance was also measured as a function of temperature for samples grown on STO. In order to determine the critical temperature of the described transition, resistance of the thin film at different temperatures (from 300K to 50K) using a 4-points probes method has been measured. The critical temperature for YBCO thin films is about 90K, so this is an appropriated range of temperature to study. With these measurements, critical temperature (T_c) and the transition width (ΔT_c) can be determined.

III. RESULTS AND DISCUSSION

A. Crystalline structure

The θ - 2θ scan of samples has given information about the out of plane crystalline structure. This information is shown in the diffractograms shown in figures 2 and 3.

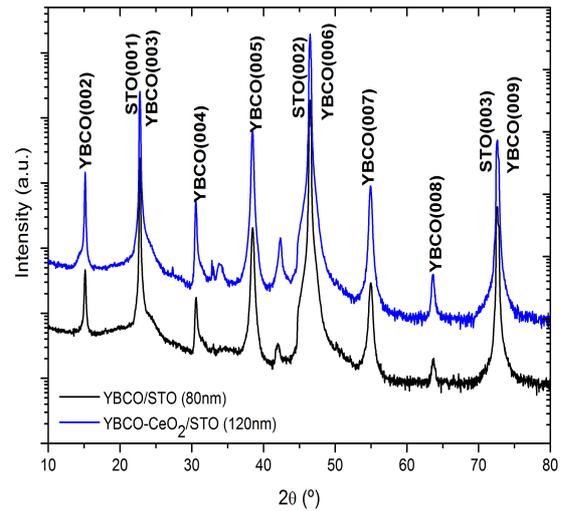


FIG. 2: Diffractograms of 2θ - ω scans of samples grown on STO.

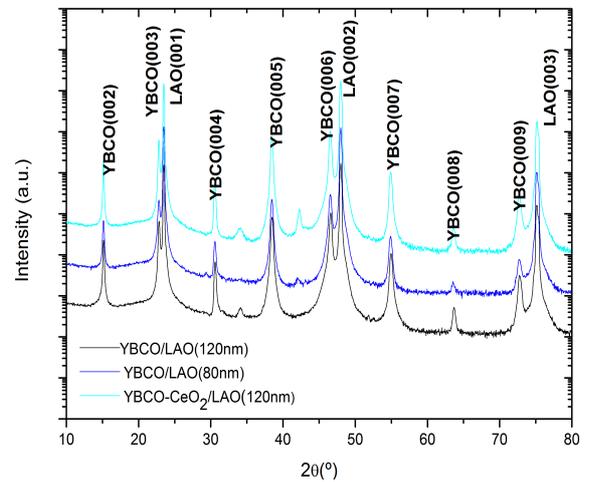


FIG. 3: Diffractograms of 2θ - ω scans of samples grown on LAO.

Figure 2 shows the intensity Bragg peaks of an YBCO sample of 80 nm of thickness (bottom) and YBCO-CeO₂ of 120 nm of thickness (top) on STO(001) substrates. YBCO peaks corresponding to c-orientation are identified in both samples. Figure 3 shows the intensity Bragg peaks of an YBCO sample of 120 nm of thickness (bottom), YBCO of 80nm thickness (middle) and YBCO-CeO₂ 120 nm thickness (top) on LAO(001) substrates. On LAO samples can also be identified c-axis oriented YBCO peaks. There are some non-identified peaks in all samples, but they don't correspond to any YBCO reflection. These peaks are present in all samples, so the effect of doping doesn't affect the out of plane crystalline structure.

In order to know if films are epitaxial in plane crystalline structure must be analysed by an XRD Φ -scan around asymmetrical reflections. This scan has been realised using the YBCO(308) reflection. Figures 4 and 5 show the diffractograms obtained in the measurements.

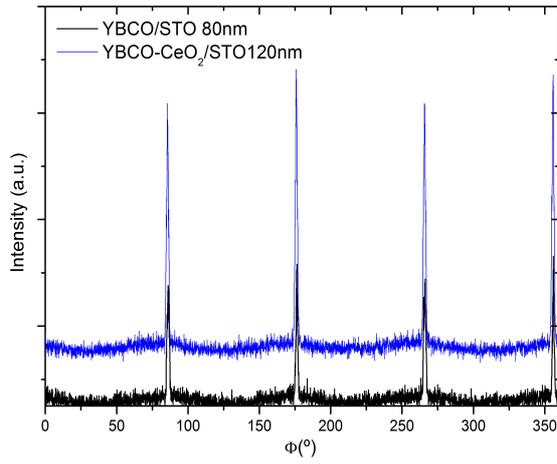


FIG. 4: XRD Φ -scan around asymmetrical YBCO(308) reflection for samples grown on STO.

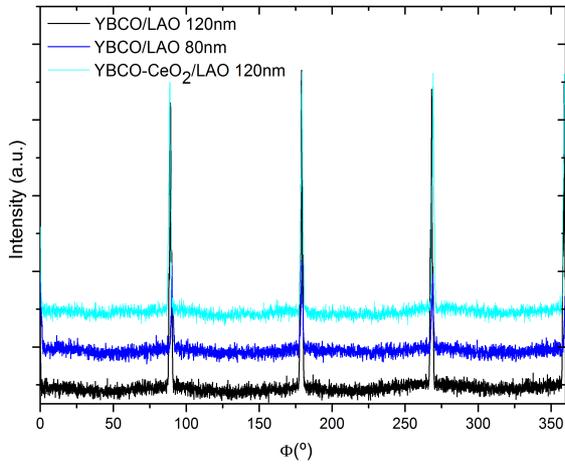


FIG. 5: XRD Φ -scans around asymmetrical YBCO(308) reflection for samples grown on LAO.

Figures 4 and 5 show the diffractograms obtained measuring a Φ -scan around asymmetrical YBCO(308) reflection for samples grown on STO and LAO respectively. In both diffractograms there are four peaks spaced with a periodicity of 90° , demonstrating in plane order. These scans confirm the epitaxial growth.

B. Morphology

Using AFM in contact mode and analysing the results using WSxM software of Nanotec[6] the images shown in figure 6 were obtained. The samples look uniform. There are not many differences between films on LAO and films on STO. The roughness of the surface of samples has been quantified by the root mean square (RMS) value. The roughness of the samples is quite large, but YBCO thin films usually rough [7]. In our study, the RMS values in YBCO thin films decreases with the thickness of the sample (number of pulses) in STO samples but in LAO samples, the roughness decreases when the thickness of the sample is larger.

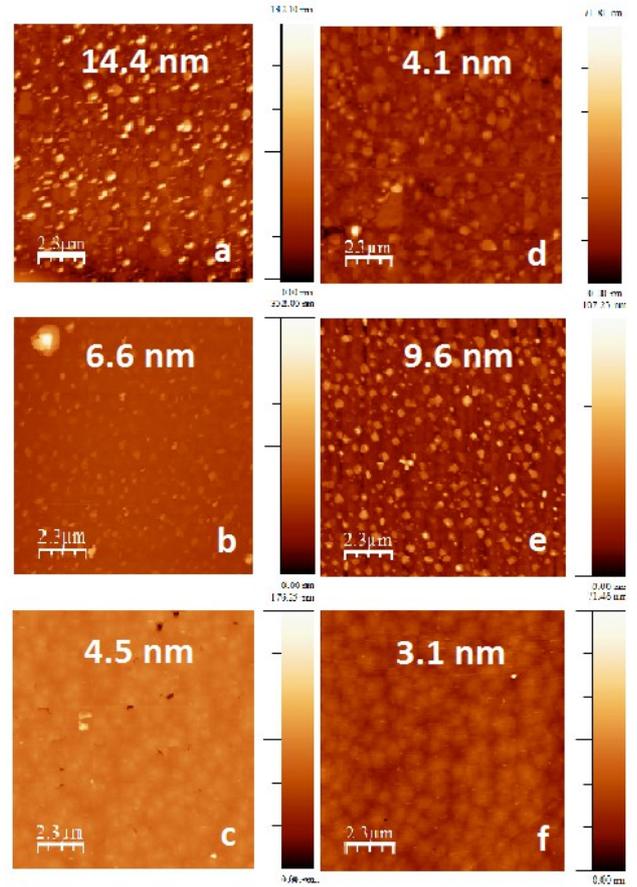


FIG. 6: Morphology and RMS value (top) of a) YBCO 120nm on STO, b) YBCO 80nm on STO, c) YBCO-CeO₂ 120nm on STO, d) YBCO 120nm on LAO, e) YBCO 80nm on LAO, f) YBCO-CeO₂ 120nm on LAO.

Remarkably, it is found that YBCO-CeO₂ samples have lower RMS values than pure YBCO thin films. It means that with the addition of CeO₂ nanocrystals, we achieve a smoother surface in both substrates.

C. Electrical transport properties

The dependence of the electrical resistance with the temperature is interesting to study because it is the first analysis to study the superconductivity and it allows to determine the critical temperature. The resistance of our samples was measured in a range of temperature between 300K to 50 K because is well known that YBCO in bulk form has it's transition to a superconducting state around a temperature of 90 K. Figure 7 shows the results of the resistance measurements for all the thin films grown on STO substrates.

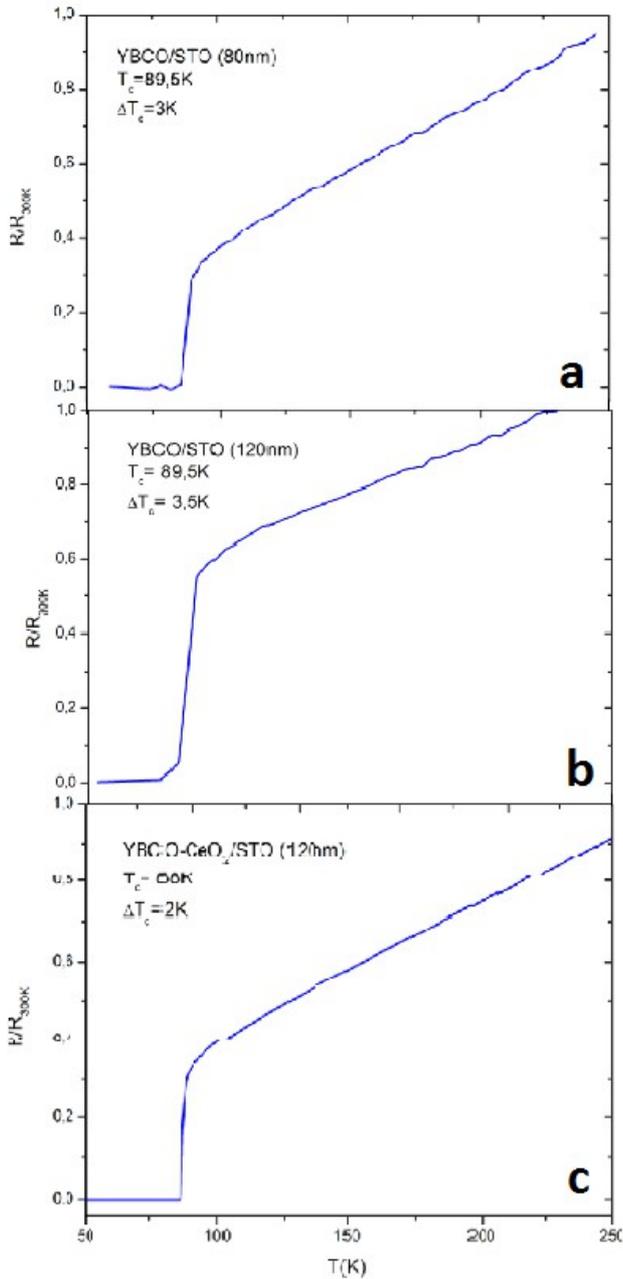


FIG. 7: $R(T)$ measurements of a) YBCO 80nm, b) YBCO 120nm, c) YBCO-CeO₂ 120nm

All samples have the transition to superconductor at temperatures closely below 90 K and with narrow transitions of about 2 K. Table II collects the results of critical temperatures and the width of the transitions.

Sample	T_c (K)	ΔT_c (K)
YBCO/STO 80nm	89.5	3,0
YBCO/STO 120nm	89.5	3,5
YBCO-CeO ₂ 120nm	88.0	2,0

TABLE II. T_c and ΔT_c of samples grown on STO.

The critical temperature had not decreased significantly in YBCO-CeO₂ nanocomposite thin film. It has only decreased 1.5 K, that is insignificant if the width of the transition (determined by ΔT_c) is considered, because the transition of YBCO-CeO₂ becomes narrower than YBCO's.

IV. CONCLUSIONS

YBCO-CeO₂ nanocomposite films have been successfully grown on STO(001) and LAO(001) using Pulsed Laser Deposition, maintaining and even improving some of YBCO's properties. Epitaxial growth was confirmed by the XRD measurements and no differences were appreciated between the nanocomposites and pure YBCO thin films, however, the surface structure has significantly changed. AFM scans analysis have revealed a decrease of the surface roughness in nanocomposite films in comparison with single YBCO films. The electrical transport properties measured have not changed by adding CeO₂ to YBCO: YBCO-CeO₂ films are still superconducting below a temperature of 90 K.

In summary, the effect of adding CeO₂ does not degrade YBCO's properties. It would be interesting to study if the critical current J_c is higher in those samples as it increases in samples when CeO₂ nanocrystals are added, but this study has not been realized yet.

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