

# SUPERCONDUCTING NANOCOMPOSITE FILMS

# **GROWN BY CHEMICAL SOLUTION DEPOSITION:**

# SYNTHESIS, MICROSTRUCTURE AND PROPERTIES

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### **TESI DOCTORAL**

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"First, comes the synthesis"

J.Corbett

### LIST OF ACRONYMS

BZO	BaZrO <sub>3</sub>
dofm	Distance of Matching
EDX	X-ray energy dispersive spectroscopy
EGA	Evolved Gas Analysis
FIB	Focused Ion Beam
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full-Width Half-Maximum
Hc	Critical field
HR	High resolution
HRDRX	high resolution X-ray diffraction
HTS	high temperature superconductors
Jc	Critical current density
LAO	LaAlO <sub>3</sub>
MS	Mass Spectrometry
NC(s)	nanocomposite(s)
Np(s)	Nanoparticle(s)
OD or ODF	Orientation Distribution (Function)
QPA	Quantitative Phase Analysis
QTA	Quantitative Texture Analysis
RE	Rare earth
SEM	Scanning Electron Microscopy
SQUID	Superconducting Quantum Interference Device
STO	SrTiO <sub>3</sub>
Tc	Critical temperature
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
W-A	Warren Averbach
W-H	Williamson Hall
XRD	X-ray Diffraction
YBCO	YBa2Cu3O7-8

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#### MOTIVATION

Metal oxides films have prompted much research due to their wide range of functional properties. Ionic and electronic conductivity, thermoelectricity, magnetoresistance, ferroelectricity and superconductivity are some of the functionalities most exploited.

In particular, superconductivity offers powerful opportunities for satisfying the present increasing energy demands. The capacity, reliability and efficiency of the electrical grid can be dramatically improved by using superconducting wires and other superconducting devices (e.g. transformers, fault current limiters or generators). Although technology exists, significant barriers remain to achieve the full potential of superconductivity to be competitive with the conventional copper devices. These barriers are related to performance and costs.

Nowadays, research in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-b</sub> (YBCO) superconducting films is basically focused in improving its performances by means of nanostructuring processes. Current-carrying capabilities are strongly enhanced if well-controlled nanometric defects are present inside the epitaxial superconducting matrix acting as vortex pinning centers. So the trick is to achieve a single-crystal like YBCO layer featuring imperfections at the nanoscale level. Moreover, and taking into account the production costs, the challenge is to achieve a cost-effective YBCO conductor using high throughput deposition processes.

Chemical Solution Deposition (CSD) is coming to prove being a very promising technique to obtain high performance YBCO conductors with lower costs than the typical *in situ* deposition techniques (i.e. vapour deposition). However, a detailed understanding of the multiple chemical and physical aspects involved in CSD is still far from being achieved. In addition, achieving structural and compositional control at the nanoscale requires of a deep understanding of all steps of CSD process, including the chemical precursor decomposition. However, despite the wide use of the trifluoroacetate (TFA) precursors in the preparation of YBCO films, the chemical decomposition reaction is still unknown as well as its influence on the final structural properties of the film. So, in this context, the first goal of the present work has been the study of the CSD process, in particular the decomposition of the metal-organic precursors. The second objective concerns the improvement of the superconducting performances of YBCO conductors by nanostructuring approaches. In particular, the main goal has been the preparation of novel YBCO nanocomposite films (i.e. YBCO + nanoparticles of a secondary phase) by cost-effective Chemical Solution Deposition (CSD) processes. Challenges in engineering the nanostructures for the best performance are to determine which ones are beneficial and tailor their density to produce the desired effect without obstructing the current flow. In addition, finding a correlation between the embedded nanostructures and the vortex pinning properties is also a key goal in order to design new nanocomposites satisfying specific applications (e.g. controlled anisotropy of the current transport).

The nanostructuring approach used in this work is based on the modification of the precursor solution by adding metal-organic salts which after reaction spontaneously nucleate forming dispersed nanoinclusions within the YBCO film matrix The microstructural characterization of the YBCO matrix as well as the study of the texture of the nanoinclusions by means of XRD has become a decisive issue in this work aiming to find the correlation with the enhanced properties achieved.

This Thesis is divided into six main chapters. First chapter is devoted to introduce YBCO superconducting films and tapes, including the fundamentals of CSD. Basics of microstructural analyses through XRD are also briefly depicted in the introductory chapter. The synthesis of the precursor solutions and nanocomposite films are presented in Chapter 2 together with the experimental techniques used throughout this work. Chapter 3 is dedicated to the study of the chemical and physical aspects of the metal-organic decomposition step of the CSD process. And finally, chapters 4, 5 and 6 are focused on the detailed characterization of the nanocomposites from phase-structural, textural, microstructural and physical point of view. This thorough characterization leads to concluding correlation between the physical properties and the YBCO microstructure (chapter 6).

For the sake of completeness, it is also included one appendix which expands on the basis of XRD line broadening models.

## 1. Introduction

Metal oxides have prompted much research in fields like physics, chemistry and material science due to their wide range of functional properties. Ionic and electronic conductivity, thermoelectricity, superconductivity, electrochromism, magnetoresistance, magnetism, piezoelectricity, ferroelectricity, and resistance switching are some of the functionalities most exploited. Consequently, metal oxides are used in a plethora of applications such batteries, electronic, energetic and memory devices.

Generally, optimal performances require of the metal oxides be in form of epitaxial films [1] that is, the metal oxide crystallites being highly crystalographically oriented on top of a singlecrystal substrate. Therefore, initially, scientific research was focused on the optimization of the thin film device configuration as well as on the comprehension of structure-texture-stress-properties interrelationships.

Nowadays the interest in functional oxides is advancing toward the generation of new or improved functionalities by means of nanostructuring processes. The strong interaction between the "host"-film matrix and the "guest"-nanostructure (typically nanoparticles or nanocolums of a secondary phase) yields to novel interfacial and coupling effects which cause the new or enhanced functionalities [2-5]. For instance, BaTiO<sub>3</sub>-CoFe<sub>2</sub>O<sub>4</sub> nanocomposite films showed coupling between the ferroelectric and magnetic order parameters of both phases via interfacial mechanisms. Another example is found in La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub>-MgO nanocomposite films in which the tuning of

electron transport properties was achieved through the stress coupling between both phases. Enhancement of ionic conductivity is also believed to be related with interfacial and size effects based on the distorted defect chemistry at the interfaces between the two phases [6].

Nanocomposites are also very promising in the area of thermoelectric materials, because of the reduction of thermal conductivity due to interface scattering thus enhancing the thermoelectric performances [7]. Yet another example, in this case dealing with resistive random access memory devices (RRAM) in which resistance switching properties (from high resistance state to low resistance state) were enhanced in metal oxide nanocomposite films like Au-ZrO<sub>2</sub> or Ag-ZrO<sub>2</sub> [8].

In the particular case of superconducting materials, it has been reported that insulating oxide nanoparticles or nanocolumns (e.g. BaZrO<sub>3</sub>, BaSnO<sub>3</sub>) embedded in a superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> film matrix extremely improve the performances at high magnetic fields [5,9,10]. As it will be discussed thorough this Thesis, lattice distortions due to interfacial effects are crucial for such improved functionalities [11].

#### 1.1. Superconductivity

Superconductivity (i.e. absence of electrical resistance below a transition temperature T<sub>c</sub> (critical temperature)) was discovered in mercury, almost 100 years ago (1911), by K. Onnes. During one century, the same phenomenon has been observed in many other metals as well as in a large number of metallic alloys and compounds. Figure 1-1 shows how T<sub>c</sub> values, of the discovered superconductors, have changed with years. Reasonably, those materials with higher T<sub>c</sub> are preferred for applications. In particular, copper oxide-based superconductors (known as cuprates or High-T<sub>c</sub> superconductors, HTS) are the most promising for zero-resistance devices because they can operate with liquid nitrogen cryogenics (77K).

Of particular interest is the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-0</sub> phase, discovered in 1987 [12], with T<sub>c</sub>=92K and bismuth-based superconductors such as Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> with T<sub>c</sub>=110K, discovered one year later [13]. An important property of both superconductors (as type II superconductors they are) is the fact that the magnetic field penetrates into the material forming quantized cylindrical flux lines called vortices. Consequently, these superconductors have the ability to carry high currents in external applied magnetic fields, which is important for most practical applications. Vortices appear in the so-called mixed state which is delimited by two critical fields (H<sub>c1</sub> and H<sub>c2</sub>) as showed in Figure 1-2.



Figure 1-1: T<sub>c</sub> vs. year of discovery of the superconductor.



Figure 1-2: Magnetic phase diagram for type II superconductors.

Vortices are characterized by a normal core of radius  $\xi$ , which is surrounded by a region of larger radius  $\lambda$ , in which superconducting currents are flowing, as it is illustrated in Figure 1-3. The values of  $\xi$  and  $\lambda$  depend on the material. The circulating currents confine the flux lines of the applied magnetic field to the vortex region in such a way that each vortex carries exactly one magnetic flux quantum,  $\Phi_0 = 2.07 \times 10^{-15} \text{ Tm}^2$ . The presence of vortices ensures an elevate number of normal-superconductor interfaces in type II superconductors.



Figure 1-3: Schematic visualization of a vortex along with the representation of the spatial decay of the magnetic field, the screening currents and the superconducting order parameter.

As the field increases from H<sub>c1</sub> to the upper critical field, H<sub>c2</sub>, (Figure 1-2) more and more vortices are introduced in the superconducting material. Eventually, at the upper critical field, the transition into the normal state occurs. At that point, the magnetic field penetrates the material uniformly throughout, and all superconducting properties are lost.

However, the capability to transport current with zero resistance is limited already in the mixed state due to the vortices motion. When a current (J) circulates through a superconductor in the mixed state, it arises a Lorentz-like force acting on the vortices [14], FL=J×B. As a result, the vortices move within the superconductor and it appears an electric field  $E=v\times B$ , where v is the local velocity of flux lines. Taking into account the non-superconducting nature of the vortex's core, the motion of vortices cause dissipation of energy and the material is no longer able to transport current at zero electrical resistance. Therefore it exist a maximum current density that can flow in the material without dissipation, which is defined as the critical current density J<sub>c</sub>. To avoid dissipation and thus increase J<sub>c</sub>, vortices must be immobilized (i.e., v=0). Effective "vortex core" pinning centers must be non-superconducting (to reduce the vortex free energy) and their dimension must be similar to the vortex's core (i.e.  $2\xi$ ). Crystalline defects are the most common intrinsic pinning centers in superconductors, especially in HTS given that  $\xi$  is of the order of few nm. So, in contrast to T<sub>c</sub> and H<sub>c</sub>, J<sub>c</sub> is not an intrinsic property of the material and it strongly depends on the crystalline imperfections. The effectiveness of the pinning centers is expressed by the so-called pinning force. In the case the  $F_L$  equals to the pinning force ( $F_P$ ) exerted by the defects, the material will transport current without dissipation. The maximum current density without dissipation,  $J_c$  is then defined as the current that produces a Lorentz-like force  $F_L$  equal to the pinning force, i.e.  $F_P = J_c \times B$ . When the Lorentz force surpasses the pinning force, the vortices are released from the pinning centers thus dissipating energy. So, in the phase diagram one can draw the so-called Irreversibility Line (IL) (see Figure 1-4) which delimitates the region where J.≠0 from the region where J<sub>c</sub>=0 in which vortices are moving at any small applied current. In the H–T region situated above the IL, the material is found in a resistive state though the material is still in a superconducting state (kept until B<sub>c2</sub>), in the sense that the order parameter is not zero but the flux lines move reversibly with ease. On the contrary, below the IL the vortices are in a solid state where defects present in the material are effective centers for vortex immobilization, and hence the current can flow without dissipation. Therefore the H-T region relevant for technological applications of Type II superconductors is limited by the irreversibility line which is much more practically important than H<sub>c2</sub>, particularly in the case of high T<sub>c</sub> superconductors.



Figure 1-4: Phase diagram of a type II superconductor showing the irreversibility line located within the mixed state.

Among HTS, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-0</sub> (YBCO) is the material displaying the highest irreversibility line at 77K [15], thus becoming the best candidate for high field and high temperature power applications (i.e. transmission cables, motors, generators, magnets, transformers and fault current limiters).

#### 1.1.1. Structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>

The YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-b</sub> crystalline structure is based on a triple perovskite structure ABO<sub>3</sub>, shown in Figure 1-5. More precisely, the unit cell of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-b</sub> is composed by a central YCuO<sub>3</sub> cube with two adjacent BaCuO<sub>3</sub> cubes along the *c*-direction. However, this arrangement would give the stoichiometric unit formula YBa<sub>2</sub>Cu<sub>3</sub>O<sub>9</sub>, thus evidencing that oxygen vacancies are present in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-b</sub> phase. Such oxygen vacancies are located in the Y–plane (i.e. z=1/2 plane) where the oxygen sites are never occupied, allowing the O3 atoms (from the intermediate CuO<sub>2</sub> planes) get closer to the yttrium (see Figure 1-6). From a chemical viewpoint, such oxygen deficiency implies that the Cu ions are present with mixed oxidation states: Cu<sup>+2</sup> and Cu<sup>+3</sup>.



Figure 1-5: Representation of the perovskite structure. The metal ion (A) with the bigger ionic radius is located in the center of the cubic unit cell, whereas the metal (B) with smaller radius is at the vertices. Oxygen ions (in blue) occupy the central position of the cube edges.

The value of  $\delta$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>, which goes from 0 to 1, is also related to oxygen vacancies but in this case such vacancies are located at the basal plane (z=0). Depending on the  $\delta$  value, the oxygen ions in the z=0 plane can be ordered or disordered leading to two different lattices: tetragonal or orthorhombic. In the tetragonal phase, i.e. 0.5<  $\delta \leq 1$ , the oxygen ions (O1) are located indistinctly at ( $\frac{1}{2}$ , 0, 0) and (0,  $\frac{1}{2}$ , 0) being this positions equally partially (50%) occupied (Figure 1-6(a)). By contrast in the orthorhombic YBCO lattice, i.e.  $0 \leq \delta \leq 0.5$ , the oxygen ions are fully ordered onto the (0,  $\frac{1}{2}$ , 0) positions, resulting in a one-dimensional Cu-O chain parallel to the baxis [16]. In orthorhombic YBCO only O1A are occupied while the O1B sites are not (Figure 1-6(b)). YBCO lattice parameters of both tetragonal and orthorhombic phases are presented in Table 1-1.

	Tetragonal (δ=1)	Orthorhombic (δ~0,1)
a (Å)	3,865	3,823
b (Å)	3,865	3,886
c (Å)	11.852	11.684

Table 1-1: YBCO cell parameters in the tetragonal and orthorhombic phases



Figure 1-6: Crystalline structures of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>. a) Tetragonal *P*4/*mmm* phase for  $\delta$ > 0.5 and b) orthorhombic *Pmmm* phase for  $\delta \le 0.5$ .

The degree of oxygen ordering is strongly related with the superconducting properties as well as with the T<sub>c</sub> values. Considering the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> notation, for an oxygen content of x=6 the compound is in the tetragonal phase and it is insulator. Increasing the oxygen content up to x=6.5, the compound undergoes a phase transition from tetragonal to orthorhombic being the latter superconductor. Finally, raising x to 6.94, T<sub>c</sub> approaches its maximum value (~92K). Above x=6.94 the compound is over-doped and T<sub>c</sub> drops [17].

Optimum oxygen stoichiometry is achieved by processing conditions (i.e. temperature and oxygen partial pressure) and several techniques are available to evaluate the final oxygen content (e.g. thermogravimetric analysis, X-Ray Diffraction or chemical analysis).

#### 1.1.2. Anisotropic Behaviour of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-ð</sub>

In YBCO, the conductivity in the parallel direction of the basal plane is much higher (3 orders of magnitude) than along the *c*-axis [14,17]. This anisotropy is due to the laminar crystalline

structure of YBCO (typical of all the cuprates superconductors) which confers a marked twodimensional character. Consequently, the vortices' structure also manifests anisotropy. The coherence length ( $\xi$ ) and the penetration depth ( $\lambda$ ) depend on the magnetic field orientation relative to the crystallographic axis of the material. To exemplify this anisotropy, in Table 1-2 are shown the values of  $\lambda$  and  $\xi$  at T=0K when the vortex is aligned parallel to the CuO<sub>2</sub> planes (a-b planes) or parallel to the *c*-axis [14].

Table 1-2: Coherence length ( $\xi$ ) and penetration depth ( $\lambda$ ) for YBCO at T=0KYBCOc-axis directionab-plane direction $\lambda$  (nm)890135

1,6

The anisotropic YBCO character can be described within the framework of the Ginzburg-Landau approximation [18] which defines the values of the charge carrier's mass in the a-b plane  $(m_{ab})$  and in the *c*-axis direction  $(m_c)$ . It turns useful to express the anisotropy as the mass ratio  $(m_{ab}/m_c)$ :

$$\varepsilon^2 = \frac{m_{ab}}{m_c}$$
 Equation 1-1

The anisotropy is also defined with the reciprocal parameter  $\gamma = 1/\epsilon$ :

0,24

$$\gamma = \sqrt{\frac{m_c}{m_{ab}}} = \frac{\lambda_c}{\lambda_{ab}} = \frac{\xi_{ab}}{\xi_c} = \frac{H_{c1}^c}{H_{c1}^{ab}} = \frac{H_{c2}^{ab}}{H_{c2}^c}$$
Equation 1-2

, where the value of  $\gamma$  is always greater than unity. Typically,  $\gamma$  values for YBCO ranges between 5 and 8 [19].

#### 1.1.3. YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-8</sub> processing

ξ (nm)

The firsts synthesized YBCO superconductors were polycrystalline materials and showed very low J<sub>c</sub> values ( $10^2$ - $10^3$  A/cm<sup>2</sup> at 77K) which did not imply any significant improvement, as compared to Cu wire. The reason of such low performances lied in the fact that grain boundaries acted as connectivity barriers for the current flow (known as weak link effect) [20,21]. In addition, the high anisotropy in the transport properties (J<sub>c</sub>//a-b planes >>> J<sub>c</sub>//c-axis) requires of the YBCO *ab* planes (i.e. the superconducting CuO<sub>2</sub> planes) being parallel aligned along the substrate surface.

Therefore, to achieve competitive superconducting performances it is required that the YBCO crystallites are highly biaxially aligned, i.e. approaching a single-crystalline state. This requirement was fulfilled by the preparation of epitaxial YBCO films on top of (001)-oriented single crystal substrates (e.g. SrTiO<sub>3</sub>, LaAlO<sub>3</sub>, MgO), leading to J<sub>c</sub> values of the order of 10<sup>6</sup> A/cm<sup>2</sup> at 77K. The choice of the single-crystal substrate is dictated by the film/substrate lattice matching, thermal expansion coefficient matching and chemical compatibility.

High-performance YBCO films have been successfully obtained by diverse deposition techniques which can be categorized as *in situ* or *ex situ* growth techniques depending on if the YBCO phase is formed as the material is being deposited (i.e. *in situ*) or in a subsequent process (i.e. *ex situ*). *In situ* and *ex situ* films have different growth modes. *In situ* film growth is generally a non-equilibrium process in which the mobility of adatoms is via surface diffusion. By contrast, *ex situ* film growth is closer to the equilibrium being the desired crystallographic phase formed through bulk diffusion by treating the precursor film at elevated temperatures.

*In situ* YBCO film growth techniques include either physical or chemical vapour deposition techniques, such Pulsed Laser Deposition (PLD), Liquid Phase Epitaxy (LPE) or Metal-Organic Chemical Vapour Deposition (MOCVD). In turn, epitaxial films obtained via the *ex situ* approach are mainly based on Chemical Solution Deposition (CSD) methodologies though in some cases the precursor film can also be deposited through physical vapour deposition (i.e. the so-called *ex situ* BaF<sub>2</sub> method). In this Thesis, a solution-based *ex situ* deposition technique has been used.

The main advantage of the *in situ* approaches is the atomic-level control of the film growth process. In addition, recent developments of the technique have led to the deposition of large areas using a continuous process. Despite the great success of *in situ* techniques in growing long lengths YBCO coated conductors (~500 m-lengths are being nowadays produced), the major drawback is related with the costs of production. The deposition-growth system is generally complex and expensive given the requirement of high vacuum conditions and eventual laser ablation system (in PLD). In contrast, *ex situ* solution-based processing enables the continuous deposition over large areas at atmospheric pressure which dramatically reduce costs. At present, performances of YBCO films prepared either by *in situ* or *ex situ* methodologies are comparable, both leading to J<sub>c</sub> values at 77K as high as 3-5 MA/cm<sup>2</sup>.

However, the applicability of YBCO epitaxial films in power applications is limited by the brittleness of YBCO because applications such magnets, motors and power-transmission lines require a long, strong and flexible conductor. This limitation has been successfully surmounted

thanks to the development of the so-called Coated Conductors (CCs) which are based on multilayer architectures (e.g. protective layer/epitaxial YBCO layer/epitaxial buffer layers) deposited onto metallic substrates as shown in Figure 1-7(a). In CCs, the YBCO biaxial texture is induced by the underlying epitaxial buffer layer, being this latter in turn induced either by a textured metallic substrate (RABiTS technology) [22] or through the deposition process (IBAD technology) [23]. Currently, several companies are developing and commercializing long length biaxially-textured coated conductors. Figure 1-7(b)-(c) shows the architectures used by SuperPower and American Superconductors. In the former, both the YBCO layer and buffer layers were grown by in situ deposition techniques whereas in the latter (Figure 1-7(c)) the YBCO layer was obtained via ex situ (i.e. Chemical Solution Deposition). Performances displayed by these coated conductors are similar to those achieved by epitaxial YBCO films grown on top of single crystal substrates (e.g. LaAlO3 and SrTiO3). However, it should be taken into account that the metallic substrate has an inherent granularity which is inherited by the YBCO layer in coated conductors. So, considering the strong dependence of J<sub>c</sub> on the grain boundary angle, the current transport in these materials flows in a percolative way through the network of grain boundaries [15]. Thanks to the optimization of the deposition technologies (IBAB and RABiTS), such granularity has been greatly reduced. Nowadays in-plane inter-grain misorientation angles around~4° are achieved, which do not imply any significant detrimental effect in performances.



Figure 1-7: a) General multilayer architecture of coated conductors (CC). b) CC manufactured by SuperPower in which YBCO epitaxial layer is deposited by metal-organic chemical vapour deposition (MOCVD). b) CC manufactured by American Superconductors, in which YBCO is deposited by CSD (MOD-TFA).

Now, the challenge is to achieve a cost-effective and high performance coated conductor, depositing both YBCO and buffer layers by high throughput deposition processes. Chemical Solution Deposition (CSD) appears to be the best candidate for large-scale production of CCs and in general for functional oxide thin films [24,25]. The major advantages of CSD are the low investment costs of the technology, the possibility to deposit over large areas and the excellent

control of film composition on a molecular level through the control of the stoichiometry of the precursor solution. In addition, no costly vacuum system is required. However, CSD is quite a recent technique in this field with still room for optimization, knowledge and control of the several processes involved.

In this Thesis, YBCO films have been deposited by CSD, in particular by the so-called Metal-Organic Decomposition of Trifluoroacetates (MOD-TFA) which has been studied in detail (Chapter 3). Moreover, single crystal substrates (i.e. LaAlO<sub>3</sub> and SrTiO<sub>3</sub>) have been used as templates for the YBCO heteroepitaxial growth. This simpler architecture serves as a model system, being the transfer to coated conductors, a step already in progress in our group at ICMAB.

Next, it will be briefly described the fundamentals of the Chemical Solution Deposition process, making emphasis in the MOD-TFA route for the preparation of YBCO films.

#### 1.2. Chemical Solution Deposition: Metal-Organic Decomposition Route

Solution chemistry is becoming a very promising path towards low cost preparation of functional thin film and nanostructured materials [24,26-31]. CSD has already been proved to succeed in the epitaxial growth of complex oxide films (e.g. Pb(Zr,Ti)O<sub>3</sub>, Ba(Zr,Ti)O<sub>3</sub> (Ba,Sr)TiO<sub>3</sub>, BaZr<sub>x</sub>Y<sub>1-x</sub>O<sub>3</sub>, (La,Sr)MnO<sub>3</sub>, (La,Sr)CoO<sub>3</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>, etc.) with many distinct functionalities (ferromagnetic, protonic and electronic conductors, ferroelectric, dielectric, high T<sub>c</sub> superconductors, etc.) [24,32-34] displaying in turn performances competitive with *in situ* methodologies.

#### 1.2.1. Processing Steps

CSD is based on four processing steps. First, the preparation of the suitable chemical precursors which are often metal-organic salts (e.g. carboxylates). These precursors are then dissolved in appropriate solvents and mixed in a stoichiometric ratio that yields the desired composition of the final film. Compositional corrections with respect to the exact perovskite stoichiometry are often required for instance when losses occur due to the volatility of a component or due to formation of solid solutions in multicomponent films. In addition, deliberate off-stoichiometry is sometimes desired for the generation of secondary phases or native point defects. In some cases, additives such as chemical stabilizers or polymers are included during

solution synthesis to adjust the properties of the coating solution. The second processing step is the deposition of the coating solution on the substrate by mainly spin coating (laboratory scale) using a rotating substrate, or dip coating in a solution bath (industrial scale) among others. Then, the as-deposited film is dried, and the organic matter decomposed at temperatures of 300-400°C typically in oxidizing atmospheres. The as-decomposed film is a mixture of amorphous and polycrystalline intermediate phases which subsequently crystallize into the desired oxide phase at high temperatures (typically 700-800°C). The crystallized film is optionally post-annealed for further densification or microstructure manipulation.

It becomes manifest that a key goal for solution-based techniques is to achieve a detailed understanding and control of the chemical and physical aspects of the several steps involved in the process together with their mutual interrelationship.

#### 1.2.2. Metal-Organic Decomposition Route

The choice of the chemical precursor must be done considering some factors: adequate solubility in the solvent to obtain stable coating solutions, acceptable wetting of the substrate, do not produce undesired residues after decomposition and do not form cracks or other non-uniformities during thermal processing. Consequently, metal-organic compounds are very appropriate since their solubility in either polar or non-polar solvents can be regulated through modification of the organic part of the molecule, and because the decomposition of the organic fraction in oxidizing atmosphere does not leave residue [35,36]. Particularly, short-chain carboxylates (e.g. acetates) or strongly chelating  $\beta$ -diketonates (acetylacetonate type) precursors are usually selected in the so called Metal-Organic Decomposition (MOD) route. Other chemical paths include sol-gel processes which use alkoxides compounds [37] or hybrid routes [24].

MOD route is a widespread and straightforward process for the preparation of functional oxide films. However it possesses some limitations: i) possible film cracking due to the excessive weight loss and shrinkage during precursor decomposition ii) film porosity and most especially iii) the limited control of structural evolution and film microstructure. Regarding this issues, in this Thesis it has been carried out a through investigation of the chemical precursors' decomposition leading to the control of the porosity development in the resultant films (discussed in Chapter 3).

#### 1.2.3. Fundamentals of Film Crystallization

Transition from as-decomposed amorphous precursor film to crystallization of the desired oxide phase occurs through nucleation and heteroepitaxial growth processes. From a thermodynamic perspective, the driving forces governing this transformation are the energy differences ( $\Delta G_v$ ) between the amorphous and crystalline states [24]. Therefore,  $\Delta G_v$  is critical to determine the energy barriers and the rate of nucleation of distinct crystalline phases. Figure 1-8 displays a schematic diagram of the free energies of a CSD derived amorphous film and the crystalline perovskite phase, where the difference between both curves is indicative of the  $\Delta G_v$  barrier.



Figure 1-8: Schematic diagram of the thermodynamic driving force  $\Delta G_v$  for crystallization as function of temperature. The free energies of a CSD-derived amorphous film, the ideal supercooled liquid and a crystalline perovskite phase are plotted [24].

The energy barrier for homogeneous nucleation (i.e. crystals nucleate in all points of the amorphous film because there exists no preferential sites) and its dependence on driving force is given by [24]:

$$\Delta G^*_{\text{hom }o} = \frac{16 \pi \gamma_i^3}{3 (\Delta G_v)^2}$$

**Equation 1-3** 

and for the case of heterogeneous nucleation (i.e. crystals nucleate at the film/substrate interface):

$$\Delta G_{\text{hetero}}^* = \frac{16\pi \gamma_i^3}{3(\Delta G_v)^2} f(\theta)$$
 Equation 1-4

, where  $\gamma_i$  is the interface energy,  $\Delta G_v$  is the driving force for crystallization and  $f(\theta)$  a function related to the contact angle  $\theta$  with the substrate. For the case of an hemispherical nucleus,  $f(\theta)$  takes the form  $f(\theta)=(2-3\cos\theta+\cos^3\theta)/4$ .

Enhancing heterogeneous nucleation in front of homogeneous nucleation is crucial in those systems where a particular orientation of the crystal is required, as it is for example the case of epitaxial growth of thin films or interfacial nanostructures. In this case, nanometer-sized grains nucleate at the substrate/film interface and then they grow along the interface and throughout the film consuming the randomly oriented grains and thus minimizing the grain boundary energy. By contrast when the crystallization driving force is high enough, homogeneous nucleation at the bulk of the film becomes as probable as interfacial nucleation diminishing then the influence of the substrate in the film orientation. Although the  $f(\theta)$  term still results in a lower energy barrier for interfacial nucleation, when  $\Delta G_v$  is high, there is more than sufficient energy to surmount the energy barriers for all (including less energetically favourable) nucleation events. Consequently, crystallization starts at numerous sites with identical surroundings and activation energies, leading to a large number of very small crystallites thorough the film as it is the case of polycrystalline films.

Given that the crystallization driving force depends on temperature (Figure 1-8) and the thermal energy available in the system is modified via heat treatment, driving forces determining nucleation events may also change with thermal treatment. Unless rapid thermal treatment is used, film crystallization usually starts during the heating to growth temperature. Therefore, as the temperature increases, more energy becomes available to surmount the barriers for nucleation events in addition to the energetically most favourable nucleation event. Crystallization at higher temperatures results in lower  $\Delta G_{v}$ , and due to the  $f(\theta)$  term, lower energy heterogeneous nucleation events become more important.

Interestingly, these inherent features of the CSD process offer the possibility to generate specific film structures by properly tuning the evolution from the precursors to the epitaxial forms by adjusting the processing conditions. In addition, in the case of multiphases (e.g. (nano)composites films), the  $\Delta G_v$  of each phase plays a crucial role in the final orientation being then possible the tuning of the nucleation events through the crystallization temperature of the particular phase (i.e. via thermal processing or precursor chemistry). This is a major difference respect to *in situ* deposition techniques in which the nature of the growth process leaves no room for such tuning. This key feature of CSD has been demonstrated in the present work since YBCO nanocomposites with either heterogeneously and homogenously nucleated BaZrO<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>

nanocrystals have been achieved displaying dissimilar microstructures and hence performances. By contrast, the analogous nanocomposites obtained via *in situ* approaches are fully epitaxial due to the single heterogeneous nucleation.

#### 1.2.4. YBCO Films by Metal-Organic Decomposition using Trifluoroacetate Precursors

The Metal-Organic Decomposition (MOD) process was used to prepare YBCO films shortly after the discovery of high temperature superconductors. Y,Ba,Cu-carboxylate salts (e.g. acetates) were firstly used as YBCO chemical precursors, but the poor performances of the resultant YBCO films evidenced carbon contamination, primarily in the form of BaCO<sub>3</sub>.

Gupta *et al.* offered a possible solution to this problem. They found that replacing the traditional acetate organic ligand with the fluorinated one (trifluoroacetate, TFA) caused the formation of metal fluorides (e.g. BaF<sub>2</sub> instead of BaCO<sub>3</sub>) upon decomposition. Such metal fluorides were further decomposed in humid atmosphere via HF removal, leading to the conversion to the metal oxides, and ultimately to YBCO [38]. Moreover, BaF<sub>2</sub> decomposition was achieved by the water content in the gas flow, making possible then, a fine tuning of the film growth rate through the water pressure parameter.

Several modifications of the MOD-TFA route have been reported [39-46] and currently YBCO films with comparable performances to the *in situ* approaches are obtained [34,47]. The MOD-TFA process that has been used in this Thesis is described in detail in Chapter 2 (section 2.1.2.)

In spite of the wide use of the TFA precursors in the preparation of YBCO films, a detailed understanding of the mechanisms controlling the chemical precursor conversion to the final highly textured films is still far from being achieved. Many authors focused their studies on the decomposition step in order to elucidate the nature of the intermediate phases [48-50]. Such investigations led to the identification (by XRD) of BaF<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and CuO nanocrystals which were embedded in an amorphous matrix. Contrasting with these results, in our group, it has been identified (by TEM, XRD and  $\mu$ -Raman investigations) CuO nanoparticles and Ba<sub>1-x</sub>Y<sub>x</sub>F<sub>2+x</sub> (BYF) solid solution in a quasi-amorphous matrix [51].

Since YBCO pathway conversion can take place through different scenarios which are not well understood it is not straightforward to define a single chemical reaction. Therefore, it is proposed the flow chart indicated in Figure 1-9. It is worth mentioning that volatile species evolved during the TFA decomposition (unknown up to now) have been indentified in this Thesis (Chapter 3).



Figure 1-9: Flow chart of the reaction path of YBCO films from Y, Ba, and Cu trifluoroacetates.

The heteroepitaxial growth of YBCO films from the as-decomposed film was earlier studied [51,52] in our group through TEM and XRD. Results indicated that the amorphous/nanocrystalline precursor film underwent strong phase segregation during heating evidencing that the nucleation of YBCO took place exclusively at the interface with the substrate. In addition, such heterogeneous nucleation was observed to be assisted by long range diffusion within a Ba-oxyfluoride matrix rather than by reaction between different phases.

Determination of the optimal YBCO growth conditions has been widely investigated [40,53,54]. A close relationship exists between temperature, water partial pressure, gas flow and oxygen partial pressure since they control the nucleation and growth rate of YBCO, determining also its microstructure. Based on thermodynamic calculations and experimental results, Feenstra *et al.* [53] proposed a phase diagram that described the YBCO stability and the crystallographic orientation of the film with respect to the oxygen partial pressure and temperature. The phase diagram for *ex situ* films [53] is consistent with that for the *in situ* films obtained by Hammond and Bormann [55]. A similar study related to the YBCO stability was performed in our group [56] for TFA-YBCO films grown on different substrates.

#### 1.3. Nanostructured Superconductors

Nowadays YBCO coated conductors satisfy the requirements in power applications at low external fields as it is the case of transmission power cables and fault current limiters (FCL). However, performances of coated conductors fall significantly in the magnetic fields required for transformers, power generators and motors as displayed in Figure 1-10. This drop in J<sub>c</sub> is related to the vortex motion (discussed in Section 1.1), thus becoming crucial the immobilization of vortices if one wants these materials to be competitive in the above mentioned high field applications. It is noteworthy to mention that the theoretical limit of J<sub>c</sub> (based on fundamental physics) is well above the requirements of devices, indicating that there is still room for optimization.



Figure 1-10: Log-log plot showing the decay of critical current density in the presence of an external magnetic field. The requirements for devices (grey boxes) clearly exceed the present performance at this temperature thus limiting the use of YBCO CCs in high field power applications.

YBCO epitaxial films feature intrinsic pinning centers due to the crystalline defects generated during the heteroepitaxial film growth. In fact it was soon realized that YBCO films displayed J<sub>c</sub> values much higher (typically ~1-2 order of magnitude higher) than YBCO single crystals due to large density of the so-called natural pinning centers (inherent of the film growth process) [57]. So, having in mind that YBCO performances depend on the vortex pinning capabilities as well as on the good texture quality of the film; the trick is to achieve a single-crystal like YBCO layer featuring imperfections at the nanoscale level.

#### 1.3.1. Vortex Pinning Centers

Vortex pinning properties depend on the dimension, distribution and anisotropy of the defects. In addition, strain fields associated with these defects may also pin vortices. Natural pinning centers present in YBCO films are sketched in Figure 1-11. These defects are typically: oxygen vacancies, cation disorder, threading, screw or edge dislocations, in-plane dislocations, twin boundaries, antiphase boundaries, stacking faults, intergrowths, etc.



Figure 1-11: Natural defects in YBCO epitaxial films.

Nevertheless, these natural defects and the eventual associated strains are not sufficient to effectively pin the vortices at high magnetic fields (as observed by the decay of J<sub>c</sub>(H) in Figure 1-10) evidencing that there is still room for improving the vortex pinning landscape in these materials through engineering the YBCO micro(nano)structure. The challenges in engineering the defect structures for optimal performances are to determine which ones are beneficial and to tailor their density to produce the desired effect without obstructing current or deteriorating the YBCO biaxial texture.

Pinning centers can be classified on the basis of their dimensionality (i.e.: 1D, 2D or 3D defects) as sketched in Figure 1-12. However, 1D or 2D-defects can act as 3D from a vortex viewpoint and some 2D that can act as 1D all depending on the orientation of the magnetic relative to the defects. Therefore other classification criterion is based on the anisotropic pinning behaviour which is associated to the dimensionality and orientation of the defect. For instance, the so-called correlated or anisotropic pinning centers arise from extended linear or planar defects. In this kind of defects, the vortex pinning length does depend on the orientation of the magnetic field. Therefore their effect is strongest when the applied magnetic field (which determines the orientation of the vortices) is aligned to the defects. By contrast, isotropic pinning centers are

defined as those in which the vortex pinning length does not depend on the orientation of the magnetic field. Consequently, they will pin the vortices whatever be the orientation of the magnetic field. Last, the pinning strength (i.e. weak or strong) is also used to classify the pinning centers [58]. In addition, the effectiveness of these defects depends on the temperature and magnetic field. For instance, some defects may be very effective at low temperatures becoming unimportant at high temperatures.



Figure 1-12: Dimensionality of the defects acting as pinning centers. a) 1D-defects like dislocations or columnar defects. b) 2D-defects like grain boundaries or stacking faults and c) 3D-defects such as nanoparticles.

Correlation between pinning properties and YBCO defects is a key issue which is fairly unexplored but very necessary in the further design of new materials satisfying specific applications. Many research groups are involved in the YBCO performance's improvement by generating artificial pinning centers with either *in situ* or *ex situ* techniques. Consequently, a plethora of papers have been published on this topic so far [5,9,10,59-63], most of them related to *in situ* techniques. In fact at the beginning of this Thesis there was no reported work about the generation of artificial pinning centers by using solution-derived techniques which prompted the present work.

It is noteworthy to mention that the different growth modes of *in situ* and *ex situ* techniques yields to dissimilar film microstructures and thus different vortex pinning landscapes. TEM studies revealed that the *ex situ* growth mode promotes a laminar structure in contrast to the columnar structure observed for the YBCO films grown via *in situ* [64]. These different film

structures translate into a different vortex pinning behaviour. For instance, the laminar structure of *ex situ* YBCO films promotes pinning along *ab* planes primarily due to the presence of stacking faults (i.e. J<sub>c</sub> is increased when the magnetic filed is aligned parallel to the *ab* planes). By contrast, the columnar structure of *in situ* films leads to correlated defects along the *c*-axis (e.g. dislocations), thus being J<sub>c</sub> enhanced when H//*c*-axis.

The anisotropic behaviour of  $J_c$  is in fact one limitation of these materials for applications which require for instance, a rotation of the magnetic field. In most cases also, the magnetic field will not be aligned along the *ab* planes but along the *c*-axis (e.g. along the wire edges or at the end of solenoid magnets). Therefore, the challenge is not only to increase the  $J_c$  in applied magnetic fields (by generating efficient vortex pinning centers) but also to diminish the inherent  $J_c$ anisotropy by tailoring the defect structure and thus tuning the vortex pinning characteristics.

Despite the dissimilar J<sub>c</sub> anisotropy of both *ex situ* and *in situ* YBCO films is important to note that in the anisotropic parameter  $\gamma$  (Equation 1-2) remain unchanged ( $\gamma$ ~7) in both cases. So the J<sub>c</sub> anisotropy (related with the defects' structure) must not be confused with the intrinsic anisotropy of the superconductor material (related with the electronic mass, discussed in section 1.1.2).

What was above described is the scenario related with pure YBCO films and this scenario can potentially change when introducing artificial pinning centers. Therefore it will be of great importance to elucidate the contribution of the introduced defects to the vortex pinning properties. This fact will be described in Chapter 6.

As already mentioned, the small coherence length of YBCO imposes the pinning centers to be in the nanoscale (~2-5 nm). According to this, first approaches to nanostructure YBCO films were devoted to the introduction of secondary non-superconducting nanometric phases. In addition and taking into account seminal works [57,65-67] on effective vortex pinning by crystalline defects (e.g. dislocations, twin and grain boundaries, stacking faults, etc), the YBCO microstructural features derived by the presence of such nanoinclusions are an unexplored but promising way to enhance or even to control the vortex pinning properties in YBCO films.

In the next section, it will be described the state of the art of artificial pinning centers in YBCO films.

#### 1.3.2. State of the Art

First approaches to generate artificial pinning centers were applied to YBCO single-crystals. These crystals were irradiated with electrons, protons, neutrons or light/heavy ions [68-70] resulting in J<sub>c</sub> enhancements by one or two orders of magnitude due to the generation of either randomly distributed or columnar defects. Particularly, heavy ion irradiation is a widely recognized approach to generate columnar defects [71]. However, adding irradiation defects to YBCO films resulted in a marginal J<sub>c</sub> improvement given the high density of natural defects occurring in epitaxial films. In addition, irradiation of kilometre long wire is commercially unpractical.

A subsequent approach to generate defects in the YBCO matrix was based on the so-called surface decoration of the substrate. It consisted of the deposition of non-superconducting nanoparticles prior to the YBCO deposition. Such interfacial nanostructures (nanoislands) became starting points of dislocations along the *c*-axis at the initial stage of the YBCO growth, which might act as effective pinning sites for H//*c*. In addition dislocations might be formed as a result of merging of misaligned YBCO growth fronts when overgrowing the nanoislands on the substrate. Distinct examples of surface decoration by *in situ* deposition of metal (Ag[72], Ir[73]) and oxide (Y<sub>2</sub>O<sub>3</sub>[63,74]) nanoislands have been reported showing mainly *c*-axis correlated pinning defects.

Surface decoration via *ex situ* solution-based techniques has also been successful in the generation of interfacial nanostructures. A great effort has been done in our group in this field which yielded to different oxide interfacial nanostructures (BaZrO<sub>3</sub>, Ce(Gd)O<sub>2</sub>, (La,Sr)O<sub>3</sub>) [29,75,76]. YBCO films were deposited on top of these decorated surfaces by MOD-TFA. In all cases a similar type of vortex pinning behaviour was observed, that was an increase of *c*-axis correlated pinning and the consequent increase of pinning force when H//*c*-axis.

Besides "decorating" the substrate, the modification of the underlying buffer layer's roughness has proved also to disrupt the YBCO matrix due to outgrowths (e.g. CeO<sub>2</sub> [77]) enhancing consequently the vortex pinning.

Although all the above mentioned interfacial nanostructures improved significantly the YBCO performances, these are still well below the specifications for in-field applications. A logical evolution of surface decoration was the incorporation of non-superconducting nanoparticles within the bulk of the YBCO film (hereafter called YBCO nanocomposites). The choice of the inclusion phase must consider several requisites: i) high stability at the YBCO growth temperatures,

ii) chemical compatibility with the underlying buffer layer, iii) no chemical reactivity neither with YBCO nor with intermediate phases of YBCO which would led to off-stoichiometries, and iv) no cationic substitution into the YBCO lattice which would diminish T<sub>c</sub>. Examples of suitable phases are: Barium perovskites (BaBO<sub>3</sub>) where B=Zr, Sn, Ir and Hf [5,9,62,78] binary rare earth oxides (RE<sub>x</sub>O<sub>y</sub>) and their solid solutions with RE= Y, Gd, Ho, Er, Dy [64,79-82] intermediate phases of YBCO like YBa<sub>2</sub>CuO<sub>5</sub> [59] and pyrochlore type rare earth tantalates (RE<sub>3</sub>TaO<sub>7</sub>) with RE= Er, Gd, Yb [83]. It must be mentioned, that not only the nanoparticles themselves were effective vortex pinning centers, given its dimensionality and distribution. Also the interaction with the surrounding highly elastic YBCO matrix plays a crucial role in the generation of artificial pinning centers.

Since the apparition of the first YBCO nanocomposite (YBCO-BaZrO<sub>3</sub> via *in situ*) in 2004 [9] a large number of YBCO films have been prepared based on the above mentioned nanoinclusion's phases, grown on single crystal substrates or onto metallic tapes. Outstanding performances were soon achieved [5,9,11,59,78] either with *in situ* or *ex situ* techniques. However, the different nature of the growth process led to dissimilar nanostructures regarding its morphology, distribution, self-assembly and texture; thus being the YBCO microstructure differently distorted. As a consequence, it was found that the anisotropy of the pinning centers strongly depended on the nanocomposite's growth mechanism. A plethora of papers have been published on this topic, most of them related with *in situ* techniques. *Ex situ* YBCO nanocomposites, the less explored ones will be the body of this Thesis.

#### 1.3.2.1. YBCO Nanocomposites via In Situ Techniques

The experimental preparation of YBCO nanocomposites by *in situ* techniques is based on the modification of the YBCO target by adding a fine dispersion of the dopant phase (mixed single target) or by switching two targets (YBCO target + dopant target).

The common feature of all *in situ* nanocomposites is the epitaxiality of the embedded nanoparticles leading to coherent or semi-coherent interfaces. Minimization of interfacial energy usually involve the generation of lattice defects (typically misfit dislocations) and lattice distortions [84].

Depending on the particular phase and deposition conditions, the embedded epitaxial nanoparticles may appear homogeneously dispersed within the YBCO matrix forming quasi

multilayers, nanoparticles or nanodisks (e.g. Y2O3 [79,85], BaZrO3 [9], YBa2CuO5 [59]). An example of YBCO nanocomposite with BaZrO3 nanoparticles dispersed at random within the film is shown in the cross-section TEM image of Figure 1-13(a). However, the most commonly observed and the most studied system is that which the nanoparticles undergo a self-assembling process leading to homogeneously dispersed vertical nanostructures or nanorods (Figure 1-13 (b-c)) which extend through the whole film thickness (e.g. BaZrO<sub>3</sub> [5,60,86,87], BaSnO<sub>3</sub> [10,78]). Combination of both nanostructures have also been reported in RE3TaO7 [83] and BaZrO3 [88] as well as coexistence of BaZrO<sub>3</sub> nanorods and Y<sub>2</sub>O<sub>3</sub> nanodisks [80,85]. The occurrence of vertical nanorods, horizontal nanodisks or simply randomly dispersed nanoparticles depends on the growth kinetics of the growth process as well as on the lattice misfit between both phases. For instance, slow growth rates and high growth temperatures allow sufficient time and mobility for the minor phase species to migrate along the YBCO surface. Minimization of eventual large misfit strain (i.e. 9% in the case of YBCO-BaZrO<sub>3</sub>) will be the driving force for the vertical assembly along with kinetic control of the growth process. By contrast, rapid growth rates and low growth temperatures do not provide enough mobility to the minor phase species and so nanoparticles mostly nucleate at random within the YBCO matrix.

Regarding the superconducting properties, *in situ* nanocomposites demonstrated enhanced in-field performances compared to pure YBCO films though T<sub>c</sub> was diminished in the case of barium perovskites and YBa<sub>2</sub>CuO<sub>5</sub> nanoinclusions ( $\Delta$ T~2-5K depending on the concentration). The reason of such T<sub>c</sub> deterioration is still controversial though it is believed to be related with the stress induced in the YBCO lattice by the highly lattice mismatched interfaces [89] (misfit~6-9%). Accordingly less mismatched interfaces (e.g. Y<sub>2</sub>O<sub>3</sub> and Gd<sub>3</sub>TaO<sub>7</sub> with misfits of -2.7% and 2,4% respectively) did not show any deterioration of T<sub>c</sub>.

As a general trend, nanorod-like structures show better in field-performances when the magnetic field is aligned parallel to them (i.e. //*c*-axis), in a way that the magnetic flux lines get pinned by the nanorods themselves. Accordingly, the degree of linearity of the rod is strongly related to the pinning capabilities. BaSnO<sub>3</sub> nanorods showed straighter portion than BaZrO<sub>3</sub> (Figure 1-13(c)) and consequently in-field performances when H//*c*, were better for the formers. In fact, YBCO-BaSnO<sub>3</sub> nanocomposites (4 wt% BaSnO<sub>3</sub>) showed the highest value of pinning force ever reported,  $F_P$ ~28GN/m<sup>3</sup> at 77K and H//*c*, twice the one of the homologous YBCO-BaZrO<sub>3</sub> nanocomposites [78]. In addition, the straightness of BaSnO<sub>3</sub> nanorods was preserved even in thicker YBCO films (~3µm).



Figure 1-13: TEM images of YBCO-BaZrO<sub>3</sub> and YBCO-BaSnO<sub>3</sub> nanocomposites showing the different assembling of nanoparticles. (a) Cross-section of an YBCO-BaZrO<sub>3</sub> nanocomposite with epitaxial BaZrO<sub>3</sub> nanoparticles dispersed at random and (b) nanorod-like nanocomposite with epitaxial self-assembled BaZrO<sub>3</sub> nanoparticles. (c) Cross-sectional and planar views of nanorod-like YBCO-BaZrO<sub>3</sub> and YBCO-BaSnO<sub>3</sub> nanocomposites.

Such *c*-axis correlated pinning was also observed in the case of BaZrO<sub>3</sub> nanodisks due to the presence threading dislocations (black arrows in Figure 1-13(a)) associated with the highly mismatched interfaces (~9%). However the improved performances were lower than the corresponding nanorod-like nanocomposites (shown in Figure 1-13(b,c)). By contrast YBa<sub>2</sub>CuO<sub>5</sub> and Y<sub>2</sub>O<sub>3</sub> nanodisks showed enhanced pinning when H//*ab*-planes which was related to the presence of planar defects [79,85].

So as a general trend, *in situ* nanocomposites show very effective anisotropic pinning centers. However, very recently it has been reported that a combination of BaZrO<sub>3</sub> splayed nanorods and nanoparticles have a synergetic pinning effect resulting in a J<sub>c</sub> enhancement in all directions and fields [88]. The best combination of particles and columnar nanodefects (achieved through modification of the deposition conditions) led to a  $F_P$ ~17 GN/m<sup>3</sup> which is still below to the *ex situ* YBCO-BZO nanocomposites (Chapter 6, [11]). Up to then, isotropic J<sub>c</sub> behaviours were only achieved by *ex situ* solution-based methodologies (Chapter 6, [11]).

BaZrO<sub>3</sub> (BZO) nanorods have been successfully transferred to the coated conductor technology. YBCO-BZO nanocomposites ~3µm-thick have been deposited on metallic buffered tapes via pulsed laser deposition leading to a very competitive coated conductor which meets the HTS industry's wire performance requirements [5].

#### 1.3.2.2. YBCO Nanocomposites via Ex Situ Techniques

At the beginning of this Thesis there was no reported work related with YBCO nanocomposites grown via *ex situ*, making evident the lack of knowledge in this field. Moreover, out of the superconductivity field, very few examples of functional oxide nanocomposite films prepared from chemical solutions are reported [3].

Solution-based YBCO nanocomposites reported up to now in the literature do not show as good performances as the *in situ* ones, being also their structural characterization very limited. Therefore the description of the state of the art will be brief, besides taking into account that the YBCO nanocomposites thoroughly described in this Thesis are the ones displaying better performances.

The most distinguishing feature of *ex situ* nanocomposites is that the embedded nanostructures do not perforce show a specific crystallographic orientation with the surrounding YBCO matrix given the possibility to nucleate homogeneously within the amorphous precursor matrix. By contrast, nanoparticles in *in situ* nanocomposites nucleated simultaneously with YBCO and hence they kept an epitaxial relationship. An advantage of the random orientation is that T<sub>c</sub> is not deteriorated unlike it happened with highly mismatched epitaxial nanostructures obtained via *in situ*. This fact is important since a reduction of T<sub>c</sub> degrades the critical currents at high temperatures. Moreover, the fact that the *ex situ* growth process is closer to equilibrium in contrast to the kinetic control of the *in situ* nanostructuring process yields to the spontaneous nucleation of nanoparticles at random rather than self-assembling. In addition, the different scenario of the *ex situ* growth process happen to be the key point in the generation of YBCO lattice distortions being extremely effective as isotropic vortex pinning centers (Chapter 4-6).

The preparation of solution-based *ex situ* nanocomposites takes advantage of the versatility and good stoichiometric and compositional control of the precursor solution. Nucleation of a secondary nano-phase within YBCO is mainly carried out by modification of the YBCO precursor solution. Such modification comprises either deliberate off-stoichiometries (e.g. excess of Y(TFA)<sup>3</sup> to yield Y<sub>2</sub>O<sub>3</sub>) or addition of soluble metal-organic salts containing the required cations to form the secondary phase.

YBCO nanocomposites prepared via *ex situ* comprise basically two types of embedded oxides: barium perovskites (BaBO<sub>3</sub>) where B=Zr [11], Hf [62] and binary rare earth oxides (RE<sub>x</sub>O<sub>y</sub>) and their solid solutions with RE= Y [90], Ho [82], Er [91], Dy [92,93].

Regarding the superconducting properties, the *ex situ* nanocomposites demonstrated enhanced in-field performances compared to pure YBCO films though pinning forces (H//c) are below those obtained with *in situ* nanocomposites. Only YBCO-BaZrO<sub>3</sub> nanocomposites, presented in this Thesis, have reached comparable values ~21 GN/m<sup>3</sup>(77K) (Chapter 6, [11]). However, a common feature of all the *ex situ* nanocomposites is the enhancement of the isotropic contribution to J<sub>c</sub>, indicating the generation of isotropic sites in which the vortices are pinned whatever direction of the magnetic field. The nanoparticles themselves, the associated strain fields and the isotropic YBCO lattice distortions, are believed to be the reason of the less J<sub>c</sub> anisotropy [11,82,90,92].

BaZrO<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and (Y,Gd)<sub>2</sub>O<sub>3</sub> nanoparticles have been successfully transferred to YBCO tapes. However, with exception of YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposites (grown by an *ex situ* approach but using vapour-deposited precursors) [90], the rest do not accomplish the wire performance's requirements given that YBCO film is not thick enough (typically 0,8  $\mu$ m obtained by multicoating). Films much thicker than 1  $\mu$ m are required. This limitation is the main handicap of the solution-based methodologies in contrast to *in situ* techniques.

#### 1.3.2.3. Open Issues

Despite the enhanced performances achieved by YBCO nanocomposites there are still open issues regarding their microstructural characterization and further correlation with properties. The main characterization tool used in the study of embedded nanostructures and YBCO matrix has been Transmission Electron Microscopy (TEM) which gives accurate but local information, evidencing the need of a broader picture. Understanding the overall influence of the nanoinclusions in the YBCO microstructure will lead to the development of novel nanocomposites satisfying the performances required in a controlled fashion.

An important, and up to now not considered, fact is that the crystallographic orientation of the embedded nanostructures very likely plays a role in the generation of defects. The different nature of the bonding structure leads to coherent, semi-coherent or incoherent interfaces, the latter having the highest interfacial energy [94]. Actually, the high interfacial energies of incoherent interfaces are the driving force of many phenomena such as grain coarsening in polycrystalline films and precipitate faceting [84], and they are still poorly understood. Taking into account that incoherent interfaces may arise in *ex situ* nanocomposites, turns to be crucial to accurately study the possible distortions in the YBCO matrix induced by relaxation of the high interfacial energy. This scenario becomes even more complex if the inclusions are nucleated prior to YBCO disrupting

then the layered growth of YBCO and promoting the formation of a higher concentration of growth fronts inducing defects such as antiphase boundaries, dislocations, stacking faults, etc.

Lattice defects can be studied by X-ray Diffraction (XRD) given that it is a powerful technique to perform microstructural analysis in a non-destructive and fast way. Moreover XRD is useful to asses the YBCO texture quality (which need to be maintained for optimal performances) and the texture of the inclusions. Microstructural and texture parameters obtained through XRD account for the whole irradiated sample volume giving thus a global picture, which is the main advantage to the local character of the TEM analysis. However, we remind that both techniques (TEM and XRD) should be regarded as complementary given that through XRD is generally not straightforward to identify individual lattice defects.

Given that in this Thesis we have focused on XRD to analyze the microstructure of YBCO (Chapter 6, section 6.2), the next section will be devoted to briefly introduce the fundamentals of such analysis.

#### 1.4. Microstructural Analysis by X-ray Diffraction

Ideally, the diffraction peaks from an infinite and defect-free crystal should be a Dirac delta function, i.e. without broadening. However, such ideal diffraction "lines" experimentally broaden due to microstructural parameters of the specimen.

Line-broadening related to the microstructural features is caused by two sources: i) the socalled **size broadening** due to the finite size of the coherently diffracting domains (this broadening is typically negligible above 0.1-1 micron) and ii) the so-called **strain broadening** due to nonuniform elastic distortions of the crystal lattice at the atomic level. Any kind of lattice defect distorting the periodicity of the crystal (e.g. dislocation, vacancy, stacking fault, site-disorder, antiphase boundary, poor crystallinity, compositional heterogeneity, grain boundary, etc) cause fluctuations of interplanar distances. Such fluctuations are assumed to vary with equal probability between two limit values ( $d+\delta$  and  $d-\delta$ ) and their quantification is performed by using a dimensionless quantity  $\varepsilon$ , called **microstrain** and defined as  $\varepsilon=\Delta d/d_0$ . Size broadening is constant in the direction  $d^*_{hkl}$  while strain broadening increases with the order of a reflection. This fact is used to separate both contributions to the overall broadening.
Instrumental aberrations also contribute to the line broadening thus, being the observed profile h(x) a convolution of the instrumental profile g(x) and the pure profile of the specimen f(x) [95]:

$$h(x) = g(x) \otimes f(x)$$
 Equation 1-5

Line broadening is generally quantified by the Full Width at Half Maximum (FWHM) or more accurately by the Integral Breadth ( $\beta$ ), which is defined as the width of a rectangle having the same area (A) and height ( $I_0$ ) as the line profile of interest (i.e.  $\beta = A/I_0$ ).

The first task to analyze the diffraction-line broadening (and the trickiest) is to correct the observed line profiles from instrumental effects. A careful scan of a suitable standard sample, showing minimal microstructural broadening will define the instrumental contribution to broadening. Various strategies to correct the instrumental effects have been developed using either deconvolution or convolution approaches. Deconvolution is performed in the Fourier space (known as Stokes deconvolution [96]), while in the convolution approach, the observed profile is built according to Equation 1-5 and adjusted to the observed pattern to a least-squares fitting (known as iterative approach [97]). In addition, simpler strategies exist consisting in a direct subtraction of the instrumental integral breadth to the experimental one [98].

#### 1.4.1. Size Broadening

In 1918, shortly after the discovery of X-ray diffraction, Scherrer pointed that peak widths were inversely proportional to domain sizes and to  $cos\theta$  in the  $2\theta$  space. This observation led to the well-known Scherrer equation [99], which correlates the width of a given diffraction peak with the apparent domain size along the orthogonal direction of the diffraction planes:

$$\beta_s = \frac{\lambda}{\langle D_V \rangle \cos \theta}$$
 Equation 1-6

In Equation 1-6,  $\beta_s$  is the integral breadth (at a given 2 $\theta$  Bragg angle) due to the size effect,  $\lambda$  is the wavelength used in the measurement and  $\langle D_V \rangle$  is the apparent volume-weighted domain size. Size broadening remains constant for all the reciprocal space points independently of their distance to the origin, and therefore it is independent of the reflection order.

#### 1.4.2. Strain Broadening

Line broadening due to lattice distortions varies with  $tan \theta$  in the  $2\theta$  space according to the equation of Stokes and Wilson (1944) [100]:

$$\beta_M = 4\langle \varepsilon \rangle \tan \theta$$
 Equation 1-7

, where  $\beta_M$  is the integral breadth due to the microstrain effect and  $\langle \varepsilon \rangle$  is the value of such microstrain. Unlike size broadening, microstrain broadening is not the same for all the reciprocal space points.  $\beta_M$  increases with the distance to the origin, thus depending on the reflection order.

Evidently, both size and microstrain effects may appear simultaneously in the specimen. Generally, in order to separate both contributions from the total broadening it is considered their dependency on the reflection. Models to separate size and strain broadening are divided in two main categories: ones based on profile modelling by analytical functions (Integral Breadth Methods) and others based on Fourier series (Warren-Averbach Method). These methodologies are described in the Appendix (Chapter 8).

Line-broadening models were first developed for plastically deformed metals and alloys and later they were successfully applied to other materials, including polymers and oxides. However, such methodologies have been hardly applied to YBCO superconductors. Only few reported works are found mostly related with polycrystalline or bulk samples [101]. In the case of thin films, size-strain analyses were applied solely to the film normal direction [102], thus having no information about its anisotropy. Given the layered structure of YBCO and the close relationship with properties is of crucial importance to determine the anisotropy of the microstructural parameters. Moreover in the case of the novel YBCO nanocomposites prepared in this work, the microstructural analysis takes even more relevance.

It is worth mentioning that microstructural parameters obtained from XRD models, are based solely on diffraction theory and in general they give little insight into the individual nature of the lattice defects. If physically meaningful results are required to characterize the microstructure, a realistic model must be introduced to account for the observed phenomena. This more realistic picture can be based on the anisotropy of strain and size parameters (if data of different *hkl* reflections are available) or on information obtained from complementary experiments, such as TEM or SEM.

# 2. Experimental Methodologies

In this chapter it will be presented all the experimental methodologies used in the present work. First, it will be described the experimental procedures carried out in the synthesis of precursor solutions, film deposition and further precursor decomposition to the final crystalline phases. Secondly, the experimental techniques used to characterize the physicochemical properties of the precursor solutions as well as the (micro)structure and superconducting properties of the nanocomposite films will be also depicted.

# 2.1. Experimental Procedures

### 2.1.1. Precursor Solutions

Precursor solutions used to prepare the nanocomposite films are based on the standard YBCO-TFA precursor solution which has been optimized [42] by members of the group (ICMAB). Further modification of this standard YBCO solution by addition of metal-organic salts containing the required cations led to the nanocomposite precursor solutions.

Final film thickness will depend on the nature of the solution (viscosity, metal concentration, surface tension, etc.) and the parameters chosen for the coating process. All the

solutions used in this work featured similar physico-chemical properties and were equally processed. Therefore, the resultant film thickness was reasonably invariable, within the range of 220-275 nm.

#### 2.1.1.1. YBCO Precursor Solution

The standard YBCO precursor solution, used to prepare either pure YBCO films or to be the starting point for the nanocomposite precursor solutions, consist of metal-trifluoroacetate salts, i.e. Y(TFA)<sub>3</sub>, Ba(TFA)<sub>2</sub>, Cu(TFA)<sub>2</sub> dissolved in methanol. The molar concentration of the TFA salts was respectively: 0.25M, 0.50M and 0.75M which led to the required stoichiometric ratio of 1:2:3.

Historically in the group, the synthesis of the metal-trifluoroacetate salts was carried out by reaction from commercial YBCO powder. The fact that the reactant (YBCO powder) was the same compound as the final product (YBCO film) was something astonishing, as a chemist I am. However, the reason to start from YBCO powder instead of the isolated metal-salts was related to the better reproducibility achieved. The non-stoichiometry and the water contamination (>2% in weight), which led to long purification steps, were the main drawbacks when starting from the separated salts [56]. However, during this Thesis it has been possible to optimize the synthesis of the metal-TFA salts. Therefore, in this section it will be described both procedures. First, the synthesis of the TFA salts from YBCO powder (from which the majority of the films have been grown) and then from the isolated salts with the optimized procedure.

#### 2.1.1.2. YBCO Precursor Solution from Reaction of YBCO Powder

The preparation of the YBCO precursor solution was performed in inert atmosphere due to the hygroscopic character of the resultant TFA salts. Yttrium, barium and copper trifluoroacetate salts were prepared by reaction from commercial YBCO powder (YBa2Cu3Ox, Solvay) with an excess of trifluoroacetic anhydride (Aldrich, 99%) and trifluoroacetic acid (Aldrich, 99%) as catalyst. The starting YBCO powder was dried in a laboratory stove at 100°C during 24h before use. After cooling at room temperature, 8.34g (6.25 mmol) of YBCO powder were introduced in a round vessel of 100 mL provided with a magnetic stirring and a reflux cooler. Next, 25 mL of trifluoroacetic acid, 25 mL of freshly distilled acetone and 5 mL of trifluoroacetic anhydride were successively added. The evolution of the reaction was followed by the change of colour and solubility (from black dispersion to a dark green solution). After stirring the mixture for ~55h at

50°C, the solution was cooled down at room temperature and filtered through syringe filters (Teflon membrane, with pore size 0.2 μm). Then, solvents (i.e. acetone) and residual reactants (i.e. trifluoroacetic acid) were removed by evaporation under vacuum using a rotary evaporator. The temperature of the heating bath was gently increased till reaching ~80°C. After the total evaporation of solvents and residual reactants, a green powder consisting of a mixture of TFA salts (Y(TFA)<sub>3</sub>, Ba(TFA)<sub>2</sub> and Cu(TFA)<sub>2</sub>) in a stoichiometric ratio of 1:2:3 was obtained. The final total metal ion concentration of 1.5M was achieved by dissolving the salts in anhydrous methanol and bringing the final volume to 50 mL using a volumetric flask. The final solution was stable up to six months if it was properly stored in sealed vials under inert atmosphere (N<sub>2</sub> or Ar). The physicochemical characterization of the solution will be described in section 2.2.1.

#### 2.1.1.3. YBCO Precursor Solution from Separated Salts

Yttrium, barium and copper trifluoroacetate salts were prepared starting from commercial metal-trifluoroacetate salts (Alfa-Aesar and Aldrich). In order to remove the waters of crystallization of Ba(TFA<sub>2</sub>)·xH<sub>2</sub>O and Cu(TFA)<sub>2</sub>·xH<sub>2</sub>O, a drying procedure was carried out using a thermostatic vacuum dryer (Vacuo-Temp, from Selecta) operating at  $10^{-2}$  mm Hg and T~85°C. We assumed that the salts were dehydrated when their weights (analytical scale) were found to be constant. Moreover, in the case of Cu(TFA)<sub>2</sub>, the change of colour from blue (hydrated) to green (dehydrated) was a clear signal to identify the end of the drying process. The isolated TFA-salts were then dissolved, in the appropriate ratio, in anhydrous methanol. After filtration through syringe filters (Teflon membrane, with pore size 0.2 µm), the volume was brought to 50 mL (volumetric flask) to give a final total ion concentration of 1.5M.

#### 2.1.1.4. Nanocomposite Precursor Solutions

Precursor solutions of the nanocomposites are derived from the standard YBCO-TFA precursor solution (section 2.1.1.1). We modified the YBCO-TFA solution by adding a certain amount of soluble metal-organic salts containing the required cations  $(Zr(C_5H_7O_2)_4 \text{ and } Ba(TFA)_2 \text{ for BZO and } Y(TFA)_3 \text{ for } Y_2O_3)$ . Stirring the solution in ultrasonic bath was often required in order to properly dissolve the salts added. Next, the resultant modified solution was filtered over a 0.2 µm membrane filter (Teflon) to remove dust and insoluble impurities. Finally the solutions were kept in sealed vials in inert atmosphere. The detailed description of the preparation of both YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub> precursor solutions comes next.

#### 2.1.1.5. YBCO-BZO Precursor Solution

YBCO-BZO solutions were found to be stable for ~2 weeks. Therefore we decided to prepare small volumes (2 mL-5 mL) which were deposited within 1.5 weeks. For brevity's sake, only the solution with "10 mol% BZO" will be described. We remark that it is not accurate to denominate the precursor solution as "solution with 10 mol% BZO" because BZO is not formed yet. However, we decided to use this terminology because it was the simplest way to compare nanocomposite films obtained through different methodologies in the group.

0.0556 mmol (27.11 mg) of Zr acetylacetonate (Zr(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>4</sub>, Aldrich) and an equivalent amount of Ba(TFA)<sub>2</sub> (0.0556 mmol, 20.2 mg) were added to 2 mL of YBCO-TFA precursor solution. Ba(TFA)<sub>2</sub> was not commercial but synthesized in the lab by reaction (at T<sub>amb</sub>) of BaCO<sub>3</sub> and trifluoroacetic acid (the reaction was instantaneous and the solid product was obtained after evaporation of solvents under vacuum at T~85°).

Taking into account that Zr is substituted by Y in the BaZrO<sub>3</sub> structure, an excess of Y was added in order to compensate its loss and thus preserving the stoichiometry of the solution. As we estimated that 20% of Zr was substituted by Y (i.e. BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3</sub>) the amount of Y(TFA)<sub>3</sub> required to compensate the solution was 0.0111 mmol (4.759 mg). The resultant mixture was then stirred till the complete dissolution of the salts (2 min). After filtering, the solution was placed into a sealed glass vial in N<sub>2</sub> atmosphere.

#### 2.1.1.6. YBCO-Y<sub>2</sub>O<sub>3</sub> Precursor Solution

The experimental procedure to obtain YBCO-Y<sub>2</sub>O<sub>3</sub> precursor solutions was easier as only  $Y(TFA)_3$  was added to the standard YBCO-TFA solution. The resultant solution was stable up to 1-2 months depending on the concentration. For brevity's sake, only the solution with "10 mol% Y<sub>2</sub>O<sub>3</sub>" will be described.

0.1112 mmol (47,588 mg) of Y trifluoroacetate (Y(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>, Aldrich) were added to 2 mL of YBCO-TFA precursor solution. The resultant mixture was stirred till the complete dissolution of the added salt (1 min). After filtering, the solution was placed into a sealed glass vial in N<sub>2</sub> atmosphere.

#### 2.1.2. Nanocomposite Films

The synthesis of both YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposite films was carried out applying the standard procedure for the preparation of pure YBCO films. This procedure consists of the following steps: 1) Deposition (spin coating) of the precursor solution onto a single-crystal substrate (LaAlO<sub>3</sub> or SrTiO<sub>3</sub>). 2) Metal-organic decomposition, also named pyrolysis step. 3) Phase crystallization (YBCO, BZO or Y<sub>2</sub>O<sub>3</sub>) and heteroepitaxial growth of the film, followed by an oxidation reaction, where tetragonal YBCO undergoes a phase transformation to the orthorhombic superconducting phase.

Prior to the solution deposition, the as-received single-crystal substrates (SrTiO<sub>3</sub> and LaAlO<sub>3</sub>) were treated in order to ensure smooth impurity-free single-terminated surfaces.

#### 2.1.2.1. Treatment of the Substrates' Surface

All substrates used in this work were treated as follows to ensure clean atomically flat surfaces [103]. First, as-received substrates were cleaned in successive ultrasonic baths of acetone and methanol (~5 min each) in order to remove impurities from the surface. Second, they were dried in compressed N<sub>2</sub>. Finally, the substrates were heat-treated to induce surface reorganization and to remove possible carbon-containing impurities still remaining on the surface. Substrates' annealing was carried out in a quartz tube furnace in constant oxygen flow of 0.5 L/min, which was regulated by a mass flow. They were heated at 900°C/h till 900°C; they remained 5 hours at this temperature and then they were cooled down to room temperature at 600°C/h. The thermal profile is sketched in Figure 2-1. To avoid possible external impurities, the quartz tube was cleaned prior to each treatment.



Figure 2-1: Profile of the heat treatment used for the surface-conditioning of single-crystal substrates.

Through these treatments, substrate's surface rearranges, either by diffusion or desorption of atoms, till it achieves the surface structure energetically more favourable. For vicinal (001) surfaces, the equilibrium structure exhibits atomically flat terraces separated by steps of height (n + <sup>1</sup>/<sub>2</sub>)a, where a is the lattice parameter and n=1/2, 1, 3/2, 2.... The presence of steps is due to the miscut angle  $\theta$ . There is always a misalignment from the (001) plane in the cut of the single-crystal, typically  $\theta$ ~0.1°-0.2°. As a result of this miscut, when (001)-surfaces rearrange they show a stair-like morphology as schematized in Figure 2-2.



Figure 2-2: Schematic representation of step's formation in (001)-surfaces as consequence of miscut angle  $\theta$ . Both substrates (STO, LAO) treated show steps' high of one unit cell and steps' widths of ~100-150 nm. For a better visualization,  $\theta$  has been exaggerated.

Treated SrTiO<sub>3</sub> and LaAlO<sub>3</sub> surfaces exhibited atomically flat terraces separated by one unit-cell high steps, indicative of a single-terminated surface. The particular termination achieved in our substrates was not investigated, given that the purpose of thermal treatments does not go further from obtaining clean atomically flat surfaces as similar as possible from one substrate to another one.

# 2.1.2.2. Deposition of the Precursor Solution

The deposition of the precursor solution onto the treated substrates was done by spincoating, a process in which a liquid is spread over a flat uniform surface through centripetal forces. The deposition was performed at controlled ambient temperatures (18-23°C) and in order to minimize the influence of impurities and environmental humidity, it was carried out in a glove box where N<sub>2</sub> flow permitted to keep the absolute humidity below ~3 g/m<sup>3</sup>. 14 µL of precursor solution were deposited on the treated single-crystal substrate by means of a microsyringe. Then, the spin rate was increased from 0 up to 6000 rpm in about 1 second. This angular speed was held for 2 minutes to ensure homogenous coverage of the substrate. Deposition step is crucial and thus it should be very well controlled to avoid any inhomogeneity in the as-deposited layer. Otherwise superconducting properties are dramatically affected.

## 2.1.2.3. Pyrolysis Step

The goal of the pyrolysis step is to remove the excess of solvent (i.e. methanol) from the asdeposited precursor film and to decompose the organic matter (i.e. trifluoroacetates). Consequently, a large fraction of precursor volume is eliminated during pyrolysis leading to strong film shrinkage (64% of film thickness). Tensile stress relaxation arisen in this shrinkage process may lead to highly inhomogeneous or even cracked films [104]. For this reason, a tight control of processing parameters is crucial in order to get homogeneous and smooth films after pyrolysis. If film shrinkage process is too fast the films turned out to be buckled or even cracked thus degrading the superconducting properties of the resultant films. Processing parameters such as temperature ramp and gas flow rate were previously optimized in the group in order to achieve a smooth stress relief. The resultant homogeneous surface's film is evidenced through optical microscope imaging (Figure 2-3).



Figure 2-3: Homogeneous surface of a pyrolyzed YBCO-BZO nanocomposite. Image was taken with Optical Microscopy.

It is important to remark, as well, that any impurity (e.g. dust speck) on the substrate's surface or on the as-deposited film will be detrimental on the homogeneity of the as-pyrolyzed film.

All the samples presented in this Thesis were pyrolyzed using identical thermal process, illustrated in Figure 2-4. The as-deposited film was slowly heated up to 310°C, in humid oxygen atmosphere. The reason to add water vapour to the oxygen gas flow is to prevent the sublimation of Cu(TFA)<sub>2</sub> by its hydro-stabilization [39]. The flow of humid oxygen was injected into the furnace

once the temperature reached 100°C to avoid the absorption of water in the gel film, which would deteriorate the film integrity. The set temperature (310°C) was held for 30 minutes, after which the water vapour was removed. Then the sample was cooled down to room temperature in dry oxygen gas flow.

Humid oxygen gas flow was obtained by injecting dry oxygen into flasks containing deionized water by using gas dispersion tubes. The resultant water partial pressure was ~22 mbar.



Figure 2-4: Thermal profile used in the pyrolysis process. Zone in blue indicate wet oxygen atmosphere with water pressure of 22 mbar. Oxygen gas flow rate was 0.5L/min.

#### 2.1.2.4. Film Growth Step

In a second heating process, the pyrolyzed films were crystallized into the desired oxide phase (YBCO and BZO or Y<sub>2</sub>O<sub>3</sub>) by heating up to 810°C in wet (P<sub>H2O</sub> = 22 mbar) nitrogen gas flow with an O<sub>2</sub> partial pressure of 0.2 mbar. Low oxygen partial pressure in the nitrogen gas flow was achieved using mass flow controllers which enable the controlled mixing of both gases. The total gas flow rate through the furnace was kept at 0.6 Lmin<sup>-1</sup> and the total pressure was 1.01x 10<sup>5</sup> Pa (1 atm, 1010 mbar). The exact thermal profile followed at ICMAB is schematized in Figure 2-5. The wet atmosphere is required to decompose BaF<sub>2</sub> (product of the pyrolysis) into BaO and HF, being the latter evacuated by the gas flow. The elimination of HF through the surface of the films is the limiting rate step of YBCO growth. Water vapour was introduced into the furnace at 100°C by bubbling the incoming gas through flasks containing deionized water.



Figure 2-5: Schematic thermal profile of film growth step and oxidation reaction to convert tetragonal YBCO to the orthorhombic superconducting phase. Zone in blue indicate wet nitrogen/oxygen atmosphere with a water partial pressure of ~22 mbar. Gas flow rate was 0.6L/min.

# 2.2. Characterization Techniques

# 2.2.1. Physicochemical Characterization of Precursor Solutions

The physicochemical parameters of the precursor solutions were routinely analyzed in order to assure their stability and reproducibility. Several are the parameters to control such as metal concentration, viscosity, surface tension, contact angle, water content and pH. The optimization of such parameters in the standard YBCO precursor solution was performed by members of our group. That study permitted to establish the specifications required to obtain good and reproducible YBCO films (Table 2-1).

YBCO-TFA solution specifications	
[metal]	[Y] = 0.25 M
	[Ba] = 0.50M
	[Cu] = 0.75M
Water content	<1%
pH (2% in water)	2-3
Angle of contact on (001)-LaAlO3 substrate	20-23°
Dynamic viscosity	3-5 mPa⋅s

Table 2-1: Specifications of the standard YBCO precursor solution. Control of these parameters enables to obtain stable solutions with high reproducibility.

The modified solutions (i.e. nanocomposites precursor solutions) were also characterized being their parameters within the specifications of Table 2-1.

Next it will be presented the experimental techniques used in this work for the physicochemical characterization (i.e. metals concentration and viscosity of the precursor solutions). In addition, Thermogravimetric Analyses (TGA) coupled to Fourier Transform Infrared Spectroscopy (FTIR) and Mass Spectrometry (MS) were also performed in behalf of analyzing the released gases during pyrolysis. This study will be presented in chapter 3 but the experimental details are given in this section.

#### 2.2.1.1. Metal Concentration

The concentration of metals in the precursor solutions was determined either by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or by classical titration methods. These analyses are crucial in order to assess the metal stoichiometry of solutions and eventual non-stoichiometries could be readjusted by addition of the required metallic salt.

ICP-OES analyses were performed by technicians in the Analytical Chemical Department of Univ. Autònoma de Barcelona. This technique uses the inductively coupled plasma to produce excited atoms that emit electromagnetic radiation at wavelengths characteristic of the particular element. The intensity of this emission is indicative of the concentration of the element within the sample. In order to get accurate results, the organic TFA matrix was decomposed at a T~70 °C by acid digestion in aqua regia (i.e. nitric acid and hydrochloric acid in a ratio of 1:3 respectively) for 48 hours. Several dilutions of the original TFA solution (starting volume 1 mL) were necessary to properly digest the organic matrix as well to fulfil the concentration specifications required for the analysis, which are in the order of ppm (i.e. mg/L). Routine precision values were around 5% which we consider too high if taking into account that the addition of metal-organic salts (in modified precursor solutions for nanocomposites) are within this error range. Therefore in the group, it has been recently applied the elemental analysis by classical titration methods showing lower precision values (~1%). Typical metal concentrations obtained with both methods are displayed in Table 2-1.

In contrast to ICP-OES, with classical titration methods it was not possible to simultaneously analyze the metals and it was necessary to analyze them separately thus needing more volume solution (~20 mL) as in the previous case (1mL). The analysis of the metal

concentration by classical complexometric and gravimetric methods was performed by members of our group at ICMAB.

Y<sup>3+</sup> was analyzed by complexometric titration using disodium EDTA (ethylendiaminetetraacetic acid) at a fixed pH~5. The endpoint titration was determined using xylenol orange (XO) as indicator which changed from red colour (Y-OX) to yellow (free OX). At the working pH, Cu<sup>2+</sup> could also be complexed by EDTA, thus interfering in the Y<sup>3+</sup> titration. Therefore, it was necessary to mask Cu<sup>2+</sup> by complexation with thiourea (H<sub>2</sub>NCSNH<sub>2</sub>).

 $Ba^{2+}$  was analyzed by gravimetry using potassium chromate (K<sub>2</sub>CrO<sub>4</sub> (aq)) as precipitation agent. Once BaCrO<sub>4</sub> was precipitated, it was filtered and dried till constant weight (analytical scale).

 $Cu^{2+}$  was analyzed by redox titration (iodimetry). First step was the reduction of  $Cu^{2+}$  to  $Cu^{+}$  by adding potassium iodide (KI) to the solution. This redox reaction led to the formation of (I<sub>2</sub>) which in a second step was titrated by thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>). As indicator it was used Starch ((C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>) which adsorbs I<sub>2</sub> changing colour from violet to white.

#### 2.2.1.2. Viscosity

Viscosity is an important parameter of the precursor solutions since it determines, along with the metal concentration and the deposition conditions, the final thickness of the films. Formally, viscosity (represented by the symbol  $\eta$ ) is the ratio of the shear stress to the velocity gradient in a fluid.



Figure 2-6: Viscosity ( $\eta$ ) as function of time of the TFAprecursor solution. Viscosity is extracted from the *y*intercept of the regression line with zero slope.

The viscosity of the precursor solutions was measured at room temperature with a rheometer Haake RheoStress 600. A small volume of solution (~1 mL) was deposited on the static plate of the instrument. A glass hood enclosed the whole arrangement to mitigate the evaporation of solvent. Then, the torque force needed to maintain the preset rotational speed of the rotating upper plate was continuously registered enabling the calculation of the shear stress ( $\tau$ ) and viscosity values ( $\eta$ ) by the software. Figure 2-6 shows the typical graphic obtained with these analyses. Viscosity values were determined from the constant range signal (avoiding instabilities of the instrument during the firsts seconds of the measurement) and were in the range of 3-5 mPa·s.

#### 2.2.1.3. Evolved Gas Analysis (EGA)

The study of the evolved gases during the metal-trifluoroacetates decomposition (pyrolysis step) was performed by EGA, *i.e* Thermogravimetry (TGA) coupled to Fourier Transform Infrared Spectroscopy (FTIR) and Mass Spectrometry (MS). These analyses were carried out in the Inorganic and Physical Chemistry Group of Hasselt University (Belgium) in the framework of a doctoral stay.

The thermal decomposition pathway of the TFA precursor solution was examined by means of thermogravimetric analysis (TGA) (TA Instruments TGA 951-2000) on-line coupled to a FTIR spectrometer (Bruker IFS 66, resolution: 4 cm<sup>-1</sup>) or to a quadrupole mass spectrometer (MS, Thermolab VG Fisons). Both of these techniques permit the analysis of the gases released during decomposition and they are used in a complementary manner. Gas molecules identification becomes easier with FTIR as no fragmentation occurs, but lower detection limit is achieved with MS. The evolved gases were identified on the basis of their FTIR and MS reference spectra available in the public domain spectrum libraries of NIST [105] and SBDS [106].

TGA measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Its principal uses include measurement of a material's thermal stability and composition.

**IR spectroscopy** is based on the vibrational excitation of bonds within a molecule. Types of bond excitation that can occur are: stretching (higher energy) and bending (lower energy) vibrations (Figure 2-7). Absorption of certain wavelengths of IR radiation is thus correlated with bending or stretching of specific functional groups within a molecule making possible the structural determination of the molecule.



Figure 2-7: Type of bond excitations occurred due to absorption of IR radiation by a molecule. a) symmetrical stretching, b) asymmetrical stretching and c) bending vibrations.

**Fourier transform** analysis involves irradiating the sample with the whole spectral bandwidth at one time and then detecting all frequencies simultaneously as a complex interference pattern. **FTIR** spectrometers have become commonplace in research laboratories. IR radiation, in the form of a frequency interferogram is passed through the sample, detected and then submitted to Fourier transform. This approach allows the scanning of the spectra several times within a second improving thus the sensitivity.

TGA-FTIR measurements were carried out by depositing ~20 mg of precursor solution onto the TGA microbalance and applying the standard thermal treatment (pyrolysis process) in air atmosphere (50 mL/ min). The gas flow, which is transparent to the IR radiation, is the responsible to carry the released species to the FTIR spectrometer with no delay in time between releasing and detection.

**MS** enables the determination of the mass of a single molecule and also provides further information about its structure. The basis of MS is the ionization of the target molecule (in our instrument, by bombardment with high energy electrons); i.e.  $M_{(g)} + e^{-} \rightarrow M^{+}_{(g)} + 2e^{-}$ . The molecular ion M<sup>+</sup> often undergoes fragmentations due to its instability. The different ion fragments and the molecular ion itself are then separated in the mass analyzer (quadrupole) according to their massto-charge ratio (m/z) and finally they are detected in proportion to their abundance. Figure 2-8 shows a scheme of a quadrupole mass spectrometer.



Figure 2-8: Scheme of a quadrupole mass spectrometer.

A quadrupole analyzer is made up of four rods across which an electric field is applied. By altering this field only those ions within a specific m/z range, so called 'stable' ions, are allowed to pass through the quadrupole and these ions are collected by the ion detector. In this way the quadrupole instrument acts as a mass filter.

TGA-MS measurements were carried out at an ionization energy of 70 eV and scans were performed in the range between m/z = 10 and 120 as the most important ions were expected to be situated here. ~20 mg precursor solution were deposited onto the TGA microbalance and subjected to the standard thermal treatment (pyrolysis process) in air atmosphere (50 mL/ min). In this case, coupling between TGA and MS requires of a special interface due to the different working pressures of the instruments (atmospheric pressure for TGA and vacuum, ~10<sup>-6</sup> mbar, for MS). The gases released during the TGA experiment are carried to the mass spectrometer through a heated ceramic (inert) capillary that connects both apparatus. Gas molecules are then ionized in the mass spectrometer.

All TGA-MS and TGA-FTIR analysis were performed using a dynamic atmosphere of dry or humid synthetic air (50 mL min<sup>-1</sup>). In order to evaporate the solvent (MeOH) from solution a dwell step for 60 min at 70°C was applied prior to the standard decomposition thermal profile.

#### 2.2.2. Structure, Texture and Microstructure of Thin Films

The structure, texture and microstructure of thin films have been investigated with several techniques which can be divided into two main groups: i) Microscopic techniques and ii) X-ray Diffraction techniques.

### 2.2.2.1. Microscopic Techniques

#### 2.2.2.2. Optical Microscopy (OM)

The surface homogeneity of as-pyrolyzed films was systematically investigated with an optical microscope Nikon Labophot. Images were taken at ×4 and ×10 augments. Films do not showing homogeneous surfaces (i.e. inhomogeneities, buckling, cracks...) were not subjected to further processing (i.e. YBCO growth).

#### 2.2.2.3. Scanning Electron Microscopy (SEM)

SEM provides topographical and elemental information at magnifications of 10x up to 100000x. This kind of microscope is very suitable to obtain films' surface information about grain size, preferred orientations, porosity, particle's distribution or material inhomogeneities, for example. Besides material evaluations, it is also used for failure analysis or quality control screening. Since the sample is investigated with electrons, it must conduct electricity. Observation of bad conducting or insulating samples can be achieved through coating them with a thin conductor layer such as gold.

SEM studies were carried out by a technician with a JEOL JSM-6300 SEM located at the "Servei de Microscopia Electrònica" at Univ. Autònoma de Barcelona. Attached to JEOL SEM, there was an Energy-Dispersive X-ray diffraction (EDX) spectrometer from LINK ISIS-200 (Oxford Instruments Company). A PC interface allowed the instrument to be easily operated. For routine analysis, it has been used a Philips-SEM 515 located at ICMAB.

The principle of operation of a SEM is the following: a beam of high-energy electrons (primary electrons) is focused on a sample placed in a vacuum chamber. As a result of this bombardment, electrons from the specimen are dislodged. Two types of electrons are produced as a result of the interaction between the primary beam and the specimen: backscattered electrons (BSE) and secondary electrons (SE). On one hand, BSE, with energies of the same order as the primary beam (~50 keV), provide information of the chemical composition of the sample because its energy depends on the atomic number of the specimen. On the other hand, SE, with lower energies (~20 eV), give information about the surface topography (2D). BSE and SE electrons are attracted and collected by a positively charged detector and translated into signal. To obtain the SEM image, the electron beam sweeps back and forth across the surface of the sample. The beam can be focused to a final probe diameter around 10 nm. Despite the considerable depth of penetration of the incident primary electron beam, the re-emitted electrons (as secondary and backscattered electrons) come from mean depths of 50nm-0.5µm depending on the density of the material. The surface features in this size range include extensive faceting, phase separation, morphology of crystals, precipitates and pores.

Asides from BSE and SE, characteristic X-rays are also emitted by the specimen enabling compositional information through analysis with a spectrometer.

SEM analysis has been applied routinely to characterize the film's surfaces of pure YBCO and nanocomposites film fabricated in this thesis. We have worked with an acceleration voltage of ~20kV and the images were taken at the following magnifications: 500×, 2000×, 6000× and 10000×.

#### 2.2.2.4. Transmission Electron Microscopy (TEM)

TEM analyses were carried out by members of our group at ICMAB.

TEM comprises a range of powerful techniques aimed to obtain internal structural information (arrangement of atoms, defects, etc.) of a material at the atomic scale using different imaging and diffraction techniques. TEM can also provide insight into the compositional features of the specimen if EELS (Electron Energy Loss Spectrometry) or EDX devices are attached.

TEM operates on similar basic principles to those of an optic microscope, but here electrons are used instead of light. A highly coherent beam of electrons is directed towards a thin sample (<100 nm) so that electrons can transmit through it. Ideally, the transmitted electron intensity distribution is magnified and focused by a system of electromagnetic lens into either an image or a diffraction pattern. The image can be digitalized and recorded by a CCD camera system. Contrast in a TEM image depends on the specific TEM technique and conditions used. For instance, for conventional bright field images, the darker areas correspond to those regions of the sample where fewer electrons were transmitted through (i.e. thicker or denser).

Low magnification TEM images and electron diffraction patterns were acquired with a 200 KV Jeol JEM-2011 microscope at Univ. Autònoma of Barcelona (UAB) and a 300 KV Philips CM30 microscope at "Serveis Cientifico-Tècnics" of the Universitat de Barcelona (UB). High resolution TEM images were performed at the "Serveis Cientifico-Tècnics" of the UB using a Jeol 2010 FEG electron microscope operated at 200 KV (point to point resolution 0.19 nm).

Nanocomposite thin films were cut to observe the inner part of the film (i.e. cross-sectional studies). Samples were prepared by using the mechanical tripod polisher technique followed by Ar milling [107,108]. Cross-sectional studies were performed by direct electron imaging which provided information about both the nanoparticles (shape, size, distribution, interface, domain orientation, etc) and YBCO matrix (lattice defects, domain orientation). Film's thicknesses were also inferred from cross-sectional images. In addition, electron diffraction patterns were used to identify the crystallographic orientation of the nanoparticles.

#### 2.2.2.5. Focused Ion Beam (FIB)

FIB images were taken by Dr. A. Palau from our group (ICMAB).

FIB uses a beam of gallium ions (Ga\*) to image the surface of a sample in a similar way as the electron beam in a SEM. Unlike electrons, when the primary beam of gallium ions hits the surface of the sample it sputters neutral atoms or secondary ions; and it also produces secondary electrons. The primary Ga\* beam is scanned over the surface to study, and the sputtered ions or secondary electrons are collected to form an image of the surface. As higher is the primary beam current, more material is sputtered from the surface. Hence, low primary beam currents are used for imaging, whereas high-beam operation is used to sputter or remove material from the surface (e.g. high-precision milling or cross-sectioning of a specific film area). FIB is chiefly used to create very precise cross sections of a sample for subsequent imaging via SEM or TEM. Cross-sectioning capacity of FIB was used in the present work to imaging the inner part of the films. The crosssectional images allowed the study of porosity development in as-decomposed films as well as observation of embedded nanoparticles in the nanocomposites, and determination of the film's thickness. An example of a typical cross-section of a pyrolyzed film is shown in Figure 2-9(a).



Figure 2-9: a) FIB cross- section image of a pyrolyzed YBCO film taken with b) Cross-Beam operation mode: milling with FIB and imaging with SEM.

A dual beam FIB Zeiss 1560XB located at "Centre Nacional de Microelectrònica" (CNM) in CrossBeam operation mode was used. With this mode of operation, both beams (ion and electron beams) are turned on and while the ion beam is milling a defined area, the SEM is used to image the milling process at high resolution in real time (Figure 2-9(b)). The ion beam was perpendicular to the sample surface while the electron beam formed an angle of 36°. The milling was performed at 30kV/50pA. A Field-Emission SEM (FESEM) incorporated in the same system allowed the simultaneous visualization of the cross-sectional region. The advantage of FESEM respect to a conventional SEM is that electrons are accelerated under the influence of a strong electrical voltage gradient (field) which enables to generate narrow proving beams with low or high energy. As a result, spatial resolution is improved (~ 1nm) and sample charging and damage is minimized.

#### 2.2.2.6. Atomic Force Profilometry

A part from FIB images, the film thickness (substrate-film step) was also measured with a profilometer Nanopics 2100 from KLATencor (3Å of resolution in height) located at ICMAB.

Profilometry is based on scanning force microscopy, i.e. detection of forces acting at nanometric scale between the atoms of a sharp mechanical tip (probe) and the sample's surface. The tip is mounted on a soft spring (cantilever); and surface-tip interactions are indirectly measured through deflection of cantilever. A scanner with piezoelectric components is used to move the tip and the sample relative to each other in all (x,y,z) directions.

The substrate-film step was made by chemical etching of YBCO using orthophosphoric acid diluted 1:20 in deionized water. A standard photoresist was previously deposited onto the film to protect a defined area and thus obtain a step after its removal (with acetone). The measurement of the step height was carried out in contact mode. In this mode, the probe is scanned at a constant force between the probe and the sample surface to obtain a 3D topographical map. When the probe cantilever is deflected by topographical changes, the scanner adjusts the probe position to restore the original cantilever deflection. The scanner position information is then used to create a topographical image.

Film thicknesses were in the range of 250 nm with a standard deviation of ~50 nm.

#### 2.2.2.7. X-Ray Diffraction Techniques (XRD)

Due to wavelengths of X-rays are of the same order of magnitude as the interatomic distances in solids (Å), these are used to study the internal (crystalline) structure of materials. When a monochromatic X-ray beam impinges on a crystalline sample, apart from absorption and other phenomena, it will be scattered with the same wavelength as the incident beam (coherent scattering). A diffracted beam may be defined as a beam composed of a large number of scattered rays mutually reinforcing one another (constructive interference). To do so they need to be in

phase. Two scattered rays are in phase if their path difference is equal to an integer number n of wavelengths, from which is derived the well-known Bragg law.

 $n\lambda = 2d_{hkl} \sin 2\theta$  Equation 2-1

, where  $d_{hkl}$  is the distance between atomic planes in the crystal and  $\theta$  is the angle between the incident beam and the plane surface. *n* is called the order of reflection. Diffraction will only occur if the normal to the atomic planes is bisecting the angle between the incident and the scattered beam (Figure 2-10).



Figure 2-10: Schematic view of diffraction (i.e. constructive interference of the scattered X-rays) from a set of atomic planes *hkl*. One defines a scattering vector  $K=k_e-k_i$  as the difference between the scattered wave vector  $k_e$  and the incident wave vector  $k_i$ . Diffraction will occur if the Bragg condition (Equation 2-1) is fulfilled and if the scattering vector K is parallel to the normal of the *hkl*-planes.

The number, disposition and intensity of *Bragg peaks* (or reflections) in a diffraction pattern depend primarily on the symmetry and size of the unit cell, the arrangement of atoms within it and on the nature and wavelength of the radiation used. In addition, the intensities may be affected by the orientation distribution of the coherent diffracting domains within the sample. In the case of a powder sample (i.e. aggregate of crystallites or coherent domains), the random orientation of the crystallites ensures that whatever the incident beam angle, it will be always the same volume fraction of crystallites fulfilling the Bragg condition (Equation 2-1). Therefore for powder samples, diffraction from different set of planes will always occur being thus the diffracted peaks clearly observed in a conventional  $\theta/2\theta$  pattern. Texture effects are recognized in a  $\theta/2\theta$  pattern by the enhancement of certain Bragg peaks (Inkt) and reduction or even absence of others when compared with a powder pattern. In particular, in highly oriented samples like single-crystals or epitaxial

thin films, only certain *hkl* planes are in diffraction condition and thus the diffraction pattern exhibit only one family of planes.

Applications of XRD in material science are vast, the most established being: determination of crystal structures, phase identification, cell parameters, quantitative phase analysis of mixtures, microstructural analysis and study of preferred orientation of crystallites (texture). In the last years, these studies have benefited from improved instrumentation and computing facilities (e.g. Rietveld method and pattern-decomposition techniques).

In this Thesis, XRD techniques have been systematically used to identify the phases in the nanocomposites (through  $\theta/2\theta$  scans) as well as to evaluate the texture quality of the YBCO film matrix and the texture of the embedded nanoparticles (through pole figures measurements). A part from these routine analyses, more specialized XRD methodologies together with computing facilities have been also carried out in order to deeper evaluate both the texture of the nanoparticles and the YBCO microstructure.

It is noteworthy to mention that conventional powder XRD patterns, i.e. only one single  $\theta/2\theta$  diagram, are not reliable to accurately study the texture of a sample because as already mentioned only those atomic planes lying parallel to the film surface will diffract. So, information about other possible orientations is lost. One alternative to the single  $\theta/2\theta$  scans are the so-called rocking curves, in which the 2 $\theta$  angle is fixed on a particular reflection, while  $\theta$  is rocked to give the intensity distribution. From a rocking curve measurement it is possible to determine the misorientation spread of the different coherent domains within the sample. However the limitation of rocking curves is that, again they only probe the texture in one direction. Only for perfect single-crystal like textures may the rocking curves and a single  $\theta/2\theta$  pattern give unambiguous information. Therefore, to accurately study the orientation distribution of crystallites it is necessary to bring to diffraction condition all the diffraction planes (apart form those lying parallel to the film surface). This is achieved by rotating the sample with a goniometer like the one schematized in Figure 2-11. The orientation of each individual crystallite is defined by a set of orthogonal axes fixed on that crystallite and referenced to an external coordinate system. In thin film, the external coordinate system is taken as the crystallographic directions of the substrate plane.



Figure 2-11: Schematic view of a goniometer displaying the three sample rotation angles ( $\chi$ ,  $\phi$  and  $\omega$ ) and the sample reference system (X,Y,Z).

The most straightforward method of depicting texture is the pole figure, which is a stereographic projection that maps the distribution of orientations for a specific crystallographic plane. From experimental pole figure data, it can be computed the so-called Orientation Distribution Function (ODF) which is the basis of the Quantitative Texture Analysis. Details of the ODF computation are given in the introductory part of Chapter 5.

#### 2.2.2.8. Pole Figures

In pole figure measurements, a given set of *hkl*-planes is selected by fixing the detector (2 $\theta$ ) and incident beam ( $\omega$ ) angle. Hence, the diffraction vector  $\vec{K}$  is fixed in space, as it can be seen from Figure 2-12(a). Diffraction will only occur if the normal to the selected *hkl*-plane  $\vec{N}$  is parallel to the diffraction vector. Therefore, the sample has to be tilted ( $\chi$  angle) and rotated ( $\phi$  angle).

Pole figures can be interpreted by considering the intersections of the normal to the selected *hkl*-planes with an imaginary hemisphere, situated above the sample surface as shown in Figure 2-12 (b). The projection of this hemisphere on a planar surface results in a pole figure, for which the intensity in each point is proportional to the volume of crystallites holding that specific orientation. For a random orientation of crystallites the pole figure will be featureless since the intensity will be uniformly distributed. By contrast, for an epitaxial thin film, in which only a single orientation is present, the pole figure is characterized by a discrete number of poles.



Figure 2-12: Scheme of the pole figure measurement a)  $\chi$  and  $\phi$  indicate the tilt and azimuth rotation angles respectively. b) Representation of the projection of a pole (from the *hkl*-normal) on a 2D circle with  $0^{\circ} \le \phi \le 360^{\circ}$  and  $0^{\circ} \le \chi \le 90^{\circ}$ .

Next it will be described the different XRD diffraction techniques used throughout this Thesis which were all based on reflection mode. The corresponding instrumentation will be also presented.

# 2.2.2.9. Two-dimensional X-ray Diffraction: GADDS

The diffractometer most used in this Thesis for the routine phase identification and texture evaluation was a Bruker-AXS D8 Advance, located at ICMAB, which operated with CuK $\alpha$  radiation ( $\lambda_1$ = 1.5406 Å and  $\lambda_2$ =1.5444 Å). The diffractometer was provided with a General Area Detector Diffraction System (**GADDS**). Hereinafter, we will refer to this diffractometer simply as GADDS. Operating power was 40kV and 40 mA. A complete scheme of the GADDS diffractometer is shown in Figure 2-13.



Figure 2-13: Components in GADDS system: X-ray source, X-ray optics (Göbel mirrors and collimator), goniometer and sample stage, sample alignment and monitor (laser video) and finally the area detector (proportional counter).

Thanks to the two-dimensional detector, a large range of  $2\theta$  ( $\Delta 2\theta = 30^{\circ}$ ) and  $\chi$  ( $\Delta \chi = 70^{\circ}$ ) positions can be measured simultaneously, thus reducing the total acquisition time if compared with standard point or linear detectors. Moreover a frame (i.e. the 2D-image) contains far more information than a conventional diffraction pattern because not only the crystallographic planes oriented parallel to the sample surface ( $\chi = 0^{\circ}$ ) will be detected but also those disoriented ( $\chi \neq 0^{\circ}$ ), thus providing information about the out-of-plane texture. Therefore 2D-XRD is specially indicated for samples containing both textured and randomly oriented phases (as it is the case of our nanocomposite films). For instance, thin films samples with a mixture of single-crystals, polycrystalline layers and textured layers can be measured with all the features appearing simultaneously in the diffraction frames.

GADDS is based on the same geometry of a conventional four-circle diffractometer in which one circle is used for the detector position and the other three circles for orientation of the sample. The rotation and tilt angles necessary to define the orientation of the sample were achieved by a goniometer, like the one represented in Figure 2-11.

The incident X-ray beam lies along the rotation axis of the diffraction cone (in the case of a powder sample) as sketched in Figure 2-14. The whole apex angle of the cone is twice the 20 value given by the Bragg law. For a flat 2D detector, the detection surface can be considered as a plane, which intersects the diffraction cone to form a conic section which is named diffraction ring.



Figure 2-14: Diffraction cone and the conic section obtained by intersection with the detector plane. D is the distance between the sample and the detector. We kept a constant D value (15 cm) for all measurements.

The 2D diffraction image (i.e. frame) is recorded as intensity values on a 1024 x 1024-pixel grid which give a resolution in 2 $\theta$  of ~0.03°. The determination of the diffracted beam direction involves the conversion of pixel information into the  $\chi$ -2 $\theta$  coordinates.  $\chi$  and 2 $\theta$  values at each pixel position are given according to the detector position which we kept at a constant value of 15

cm (detector-sample distance) for all measurements. The position of a pixel in the detector is defined by the (x,y) coordinates, where the detector center is defined as x=y=0. The detector center and coordinates for each pixel are determined by specific detector design calibration, and spatial correction [109].

Considering the bi-dimensionality of the detector,  $2\theta$  scans are not needed in GADDS because the  $2\theta$  range is already defined in the area detector. Thus the frames were acquired at a fixed  $2\theta$  position. In the case of a powder sample any value of  $\omega$  would satisfy the Bragg condition for the randomly oriented crystallites. However, in order to bring the different crystallographic planes of an epitaxial film to Bragg condition and thus visualize the diffracted spots in the 2D-image is required to scan in  $\omega$ . Figure 2-15(a) shows a typical GADDS frame measured by a continuous  $\omega$ -scan, starting from  $\omega = 12$  till  $\omega = 24$  during 1h. Data acquisition was performed at a fixed  $2\theta = 39^\circ$ , i.e. the detector is centered at the given  $2\theta$  value which will be the center of the frame.

Phase identification and further data analysis can be done using the GADDS software. The conversion of the 2D-frame into raw spectra is carried out by integrating the selected 2 $\theta$  range (with given 2 $\theta$  steps, typically we used steps of 0.03° along the Debye rings ( $\chi$ -integration). The area to integrate is defined by specifying the 2 $\theta$  and  $\chi$  range (blue box in Figure 2-15(a)). Resultant XRD pattern ((Figure 2-15(b)) resembles a conventional "powder pattern" but with better intensity and statistics, though the resolution in 2 $\theta$  is lower (~0.03°).



Figure 2-15: 2 $\theta$  frames taken with GADDS diffractometer through  $\omega$ -scan measurements (fixed 2 $\theta$ ). a) Box in blue shows the integration limits in 2 $\theta$  and  $\chi$  angles. b) After  $\chi$ -integration a conventional 2 $\theta$  diffraction pattern is obtained.

GADDS was also used to systematically analyze the texture of the films through the measurement of pole figures. 2D-XRD has many advantages over conventional 0D and 1D detectors because the orientation distribution of different crystallographic planes over a wide

range of tilt angles can be measured simultaneously. Therefore pole figure measurement with GADDS is reduced to single  $\phi$ -scans (0-360°) because the area detector assures enough pole figure coverage in  $\chi$  ( $\Delta\chi$ =60°) for multiple 2 $\theta$  values. In this way, the orientation relationship between different phases or between different layers can be easily revealed with the same sample rotation scan.

Pole figure measurements were carried out at certain 2 $\theta$  and  $\chi$  values which enabled the detection of both YBCO and nanoparticle's crystal poles. Typically, we fixed 2 $\theta$  at =30° and  $\chi$  at 55°). At the selected 2 $\theta$ - $\chi$  regions,  $\phi$ -scans were performed at every 1°. Such small step size is required when dealing with strong textures like the present case. Each  $\phi$  position was held for 20 seconds. As a result, we obtained 360° frames which can be viewed and evaluated using the software MULTEX AREA (form Bruker). Figure 2-16(a) shows the sum of the 360 frames acquired. Pole figures are then generated by selecting a 2 $\theta$ - $\chi$  sector in the frame of interest.



Figure 2-16: Frame view of the sum of the 360 2D-images taken with a step of 1° in  $\phi$ . b) Pole figure resulted from selecting the 2 $\theta$ - $\chi$  sector where appears the (222) pole of Y<sub>2</sub>O<sub>3</sub>.

### 2.2.2.10. Powder Diffraction: Siemens 5000

The routine acquisition of  $\theta/2\theta$  diffraction patterns to analyze the YBCO peak broadening as well as its structure (lattice parameters indexing), was done with an X-ray diffractometer Siemens D5000 in Bragg-Brentano geometry. The Cu source generated the K $\alpha$ -line radiation, at a wavelength of  $\lambda_1$ = 1.5406 Å and  $\lambda_2$ =1.5444 Å. The beam was collimated by a slit system which can be varied in order to run the experiments with a proper beam divergence. A graphite secondary monochromator installed in the reflected beam path, in front of the detector (scintillation counter), filtered the K $\beta$ -line of the Cu source. The resolution of the diffractometer in 2 $\theta$  was 0.01°.

Data acquisition was performed in the range of  $24^{\circ}$ - $70^{\circ}$  in  $2\theta$  with a step size of  $0.02^{\circ}$  at a speed of  $0.2^{\circ}$ / min (5.5 s/step). Determination of the integral breadth of the YBCO diffraction peaks was achieved by profile fitting (pseudo Voigt function) using the FullProf program.

# 2.2.2.11. Diffractometer Equipped with a Curved Position Sensitive Detector

The detailed study of the nanoparticle's texture was carried in collaboration with Prof. Daniel Chateigner in CRISMAT (Caen, France). The strategy was measuring full 2 $\theta$  diffraction patterns at multiple orientations of the sample in order to determine the Orientation Distribution Function, ODF (fundamentals of ODF are discussed in the introductory part of Chapter 5). We used a Huber 4-circles X-ray diffractometer at the average CuK $\alpha$  radiation ( $\lambda$ Cu=1.5418 Å) equipped with a Curved Position Sensitive Detector (INEL CPS 120), which spans a 120° range in 2 $\theta$  and have a spatial resolution of 0.03° (Figure 2-17). The CPS detector allowed the simultaneous recording of several pole figures and the full diffraction diagram. Tilting angles ( $\chi$ ) and azimuth twist angles ( $\phi$ ) were in the range of 0–55° and 0–355° respectively, both using 5° steps. The reason why not measuring complete pole figures (i.e.  $\chi$  up to 90°) is related with defocusing effects which cause an enlargement of the diffraction peak width as well a decrease of the intensity when  $\chi$ >60°. Complete pole figures, however can be reconstructed from the ODF.



Figure 2-17: Huber 4-circles X-ray diffractometer provided with a curved position sensitive detector which spans a range of  $120^{\circ}$  in  $2\theta$ .

The incident angle for the X-ray beam was  $\omega$ =15° and  $\omega$ =21° corresponding to the Bragg angle of (110) and (200) crystallographic planes of the cubic BaZrO<sub>3</sub>. The instrumental resolution

function was determined by a full mapping (in  $\omega$ ,  $\chi$  and 2 $\theta$  ranges) of the diffractometer space using the NIST LaB<sub>6</sub> powder standard.

The analysis of the data (plotting and Rietveld refinement) was done with the MAUD software which will be briefly presented at the end of this section.

#### 2.2.2.12. High-Resolution X-ray Diffraction

The detailed study of the YBCO microstructure on both pure YBCO films and nanocomposites was carried out through High-Resolution X-ray Diffraction (HRDRX) experiments. HRDRX measurements were carried out in CRISMAT (Caen, France) and CIN2 (Bellaterra, Spain) with a Philips MRD diffractometer operating with monochromatized CuK $\alpha$ 1 radiation. The use of a monochromator in the primer optics and a crystal analyzer in the secondary optics enabled the instrument to work at high resolution mode (i.e. resolution in 2 $\theta$  of 0.0001°). A parallel beam with 25 arc second of divergence was produced by a focusing hybrid mirror and a 4-crystal Ge-220 monochromator. The low beam divergence and the small wavelength spread produced by the 4-crystal monochromator are because the crystals are aligned such that the radiation from the source meets each crystal surface at the Bragg angle. A CuK $\alpha$ 1 emerges through a hole in the housing at C, parallel to the original input beam (see Figure 2-18). A high-resolution signal was obtained by using a channel cut triple Ge-220 analyzer. However, it must be mentioned that the low beam divergence provoke a significant decrease of counts, thus requiring longer acquisition times than conventional XRD.



Figure 2-18: The principle of Bartels monochromator.

Epitaxial thin films were oriented with an Eulerian cradle, using the common  $\omega$ , X and  $\phi$  rotation angles. In order to assure maximum diffracted intensity (i.e. we are measuring the center of the crystal pole) it is required to optimize the  $\omega$ ,  $\phi$ , and X sample positions for a given (*hkl*). This is a tedious task but crucial to obtain useful data.

Once the maximum of YBCO diffraction lines were optimized,  $\theta/2\theta$  scans were performed separately for each YBCO reflection. In this way it was possible to increase the counting time (i.e. increase number of counts in intensity) without having prohibitive experiment times. The measurements were carried out within a 2 $\theta$  range of 2-4° using 0.001° as step size and counting times of 10s/step. Operating power was 45 kV and 40 mA.

Asymmetrical reflections, with diffraction planes not parallel to the sample surface, could also be measured using the orientation facilities of the four-circle diffractometer.

#### 2.2.2.13. MAUD Program (Material Analysis Using Diffraction)

MAUD program [110] is a free software package based on the Rietveld Method [111] in which powerful algorithms for texture analysis are implemented. Isotropic and anisotropic microstructural (size-strain) models and residual stress models are also implemented. MAUD is of general application for thin films, multilayer/multiphase, textured, polycrystalline and even amorphous materials.

The software takes advantage of the systematic intensity deviations that occur in a textured material compared with a powder sample. The observed intensities are related not only to the crystal structure by means of the structure factor but they are also linked to the texture through the ODF. So, with MAUD, we can use the diffraction patterns to extract texture, microstructure and stress information in a similar way crystallographers extract structural information. This new methodology is often referred to "Combined Analysis" [112].

Data collected from GADDS (2D-images), CPS (multipatterns) and HRDRX (single peaks at different sample positions) were loaded with MAUD software. In the case of 2D images, these were converted to multipatterns through an integration procedure.

The texture was modelled through the refinement of the Orientation Distribution Function (ODF) using E-WIMV or Standard Functions formalisms. Standard Functions are specially indicated for very sharp textures with the advantage that only few parameters are needed (fiber, spherical components) which speeds up the refinement. The disadvantages are that the number and locations of components must be manually defined at the beginning of the refinement. In addition, complex textures require several components, thus several parameters. By contrast the EWIMV Method does not need any prior assumption to operate, and the texture can be obtained without introducing any parameter. However they are more time consuming. Generally we used Standard Functions to describe the texture of YBCO and the E-WIMV model for the nanoparticles.

Microstructural parameters (crystallite size and microstrain) were calculated in the program by deconvoluting the instrumental broadening (if necessary) from the experimental profile in the Fourier space, using the Lorentzian and Gaussian parts of the profile. Eventual anisotropic crystallite sizes and microstrains were modelled by applying the Popa formalism [113]. Microstructural analysis has been mainly applied to the YBCO phase.

The iterative process inside MAUD works as follows: a first Rietveld refinement is operated cyclically on multiple diffraction patterns measured for as many as necessary sample orientations. Then the integrated intensities extracted from Le Bail algorithm are used for a first refinement of the Orientation Distribution Function (ODF). The ODF obtained is then introduced in the cyclic Rietveld refinement of the XRD patterns. If residual stresses were present (not in our case), the macroscopic elastic tensors are calculated after the ODF refinement in order to correct for diffraction peak positions. The new refined parameters are used for a subsequent cycle to obtain a new ODF, and so on. In this way, the ODF refinement takes progressively account of the microstructural and structural features, while the Rietveld analysis is corrected for the texture. The operation leads to the determination of the parameters satisfying the best solution of the whole collection of measurements. The quality of the refinement was assessed by comparing the experimental and the calculated patterns either visually or through the reliability factors.

### 2.2.3. Superconducting Properties of Thin Films

The superconducting properties of pure YBCO films and nanocomposite films were performed at ICMAB by other members of the group.

# 2.2.3.1. Inductive Measurements: SQUID Magnetometer

SQUID (Superconducting Quantum Interference Device) magnetometers are instruments with high sensitivity to measure in a non-destructive way the magnetic moment of a sample, from which the magnetization and magnetic susceptibility can be obtained. The versatility of these systems permits to perform both dc and ac measurements of magnetic moments. In the present work, dc-magnetometry was used to investigate the electromagnetic response of superconducting YBCO thin films.

SQUID magnetometer consists of a SQUID-detection system and a precise temperature control. The detection system is based on a set of pick-up coils located at the centre of a superconducting coil which can provide high magnetic fields. The sample is placed inside the superconducting coil so that it is submitted to uniform magnetic fields applied parallel to its *c*-axis. During the measurement, the sample is moved along the pick-up coils. As a result, a current proportional to the magnetic flux variation is induced in them. This signal is amplified by a SQUID sensor, which acts as a highly sensitive current-voltage converter detecting voltage variations proportional to sample's magnetization. This sensor can resolve magnetic moments of the order of  $10^{-9}$  A·m<sup>2</sup> ( $10^{-6}$  emu). The whole system is placed inside a helium cryostat, which enables to refrigerate the superconducting coil and perform measurements between 5K and room temperature.

Inductive measurements were carried out at ICMAB using two SQUID magnetometers from Quantum Design provided by 5 T and 7 T superconducting coils, respectively. To ensure good homogeneity of magnetic field and temperature during measurements, displacements of the sample within the coils were not larger than 2 cm.

Figure 2-19 exhibits a typical measurement of the magnetic moment as function of the applied magnetic field H//c of a 250 nm-thick YBCO-BZO nanocomposite film. To perform these measurements, the sample was cooled down to 5 K at zero magnetic field. Then, the magnetic moment was measured as the field was increased up to a certain field  $\mu_0$ H<sub>M</sub> (lower branch) and decreased down to 0 T (upper branch).



Figure 2-19: Inductive SQUID measurement of magnetic moment as function of applied magnetic field at 50 K of a YBCO-BZO (7 mol. %) nanocomposite.

From magnetization measurements, the critical current density of the superconducting film was determined through the Bean model [114,115]. For a thin film with squared shape [116], the critical current density values, J<sub>c</sub>, can be calculated through the equation:

$$J_c = \frac{3\Delta m}{a^3 \cdot t}$$
 Equation 2-2

, where *a* is the lateral sample dimension (5 mm), *t* the thickness of the film and  $\Delta m$  the width of the saturated hysteretic circle (i.e. when the superconductor is fully penetrated and the internal field is considered similar to the applied field). Dependence J<sub>c</sub>(*H*) is obtained from the dependence of the magnetization with magnetic field, *M*(*H*).

As observed in Equation 2-2, it is indispensable to know the thickness of the films to obtain accurate J<sub>c</sub> values. Therefore, thicknesses were systematically determined either by profilometry, cross-sectional TEM, or cross-sectional FIB images.

#### 2.2.3.2. Electrical Transport Measurements

Critical current densities can also be determined from electrical transport measurements. Ideally, the critical current (I<sub>c</sub>) is defined as the maximum current that can flow in a superconductor without dissipation. When the applied current exceeds I<sub>c</sub>, the resistance becomes non-zero and a drop in voltage is measured. So, critical current densities can be determined from I-V curve, more generally from J-E curves.

Electrical transport measurements were carried out with a Physical Properties Measurement System (PPMS) from Quantum Design at ICMAB. The system essentially consists of a 9 T superconducting magnet and a helium cryostat. Precise control of temperature within the range 1.8 - 400K can be achieved. The system also has a nanovoltimeter and a dc/ac current source which can provide currents from 1  $\mu$ A to 2 A with a resolution of 0.1  $\mu$ A.

The sample was mounted in a single-axis rotor with a total angular range of  $370^{\circ}$  with a precision of 0.1°. So, the dependence of critical current densities with temperature and magnetic field intensity and orientation, J<sub>c</sub>( $\theta$ , *H*, *T*) could be investigated. Prior to measurements, silver contact pads were deposited by thermal evaporation at 10<sup>-6</sup> mbar on YBCO thin films and then annealed under oxygen atmosphere at 400°C for 1 h to ensure good electrical contacts with resistances below 10 µΩ. Afterwards, patterns with bridges of ~20 µm width and ~0.1-1mm long in four point configuration were done by photolithography [117].

In four point configuration, a dc-current was ramped till a desired value I<sub>M</sub> between two pads and the voltage was read between two other pads. These I-V curves were obtained for distinct magnetic fields and temperatures. In the present work, the current required to develop an electric field of 1  $\mu$ V/cm inside the superconductor was the criterion used to determine I<sub>c</sub> (J<sub>c</sub>).

# 3. Evolution of Metal-Trifluoroacetate Precursors during Thermal Decomposition

In spite of the wide use of the trifluoroacetate (TFA) precursors in the preparation of YBCO films, a detailed understanding of the mechanisms controlling the chemical precursor conversion to the final highly textured films is still far from being achieved. The decomposition step of the MOD process for YBCO growth, i.e. the pyrolysis process, was initially limiting the overall yield of the conductor production due to the very long duration (~ 24 h) required to keep film homogeneity. Further investigation of the stress relief mechanisms during decomposition of anhydrous TFA precursors showed that much shorter processes could be used (~ 0.5 h) [104]. Shortening the pyrolysis time requires an accurate selection of the processing parameters controlling the shrinkage process and the diffusion of exhaust gas. The poor mechanical properties of the gelified film may easily lead to the formation of defects and inhomogeneities such as cracks, blisters or film buckling, each having strong influence on the final quality of the pyrolyzed and subsequent grown films [104]. Some controversy exists, however, concerning the relevance of different parameters on the film degradation process. It has been suggested that reducing the fluorine content in the metalorganic precursors could help to lessen inhomogeneities in the resulting film (e.g. blistering [44], surface damages generated by bubbling [118] , etc.). These issues were even more critical in multideposition [119], where intermediate deposition-pyrolysis processes were added in order to fabricate films with larger thickness. In that case, phase separation at the interfaces was very often
observed showing detrimental effects on the film performance. Therefore, it is clear that a crucial point in the MOD process towards YBCO films preparation is the precursor decomposition chemical reaction. Furthermore, the identification of the released gases during TFA decomposition could sort out its possible nuisance on the final film homogeneity, microstructure and physical properties, as well as its potentially harmful environmental effects and toxicity.

The decomposition reaction of the metal-trifluoroacetates has been described by several authors with different degrees of detail [52,120,121]. Essentially this reaction is described as follows:

 $Y(CF_3COO)_3 + 2Ba(CF_3COO)_2 + 3Cu (CF_3COO)_2 \rightarrow CuO + Ba_{2-x}Y_xF_{2+x} + gaseous phases$ 

## Scheme 3-1: General decomposition reaction of the metal-trifluoroacetate precursors.

Surprisingly, however, the chemical reaction that occurs in Scheme 3-1 is poorly understood and the unknown gaseous phases have been essentially assigned [47,120] to CO, CO<sub>2</sub>, HF and  $C_nF_{2n+2}$ .

In this chapter, we present a thorough qualitative analytical study of both gaseous and solid decomposition products of the TFA precursor gel as well as the influence of the gas flow atmosphere in such products. Evolved Gas Analysis (EGA) was carried out by Thermogravimetry coupled to Fourier Transform Infrared Spectroscopy and Mass Spectrometry (TGA-FTIR and TGA-MS). X-Ray Diffraction of the resulting solid product after the thermal treatment was also performed. This study has allowed us to define for the first time a complete decomposition reaction where the gaseous phases indicated in Scheme 3-1 have been identified. Particularly, contrarily to what was widely believed, no hydrofluoric acid (HF) was detected during the pyrolysis step, which is a key point to assess the degree of chemical toxicity of the exhaust.

Porosity development in the as-decomposed films was also investigated through cross section-Focused Ion Beam (FIB) images. In the present chapter, we show the firsts results where new conditions are found to modify the precursor decomposition path resulting in a key factor to control and eliminate the porosity in these materials.

## 3.1. Thermogravimetry and Evolved Gas Analysis

The TGA-EGA measurements presented in this section were carried out in the Inorganic and Physical Chemistry Group of Hasselt University (Belgium), under the supervision of Prof. M.K. Van Bael and Dr. An Hardy. I spent two months there, granted by CSIC, in the framework of a predoctoral short stay.

The thermal decomposition pathway of the TFA precursor solution was examined by means of thermogravimetric analysis (TA Instruments TGA 951-2000) on-line coupled to either a FTIR spectrometer (Bruker IFS 66) or a quadrupole mass spectrometer (MS, Thermolab VG Fisons). All TGA-MS and TGA-FTIR analysis were performed using a dynamic atmosphere of dry or humid synthetic air (50 mL·min<sup>-1</sup>). Moreover, in order to evaporate the solvent (MeOH) from solution a dwell step for 60 min at 70°C was applied prior to the standard decomposition thermal profile.

TGA together with EGA revealed that TFA decomposition proceeds in 3 stages (Figure 3-1). The first stage (T<70°C) involves both dehydration and evaporation of organic solvents, then, at higher temperatures (70°-240°C, stage II) takes place the thermolysis of coordinated solvents. Finally, the thermo-oxidative decomposition of trifluoroacetates comprises the stage III (240°-300°C).



Figure 3-1: Thermogravimetric analysis of the TFA precursor gel in dynamic air. Three main regions according to the weight loss derivative curve (in blue): regions I and II correspond, respectively, to un-coordinated and coordinated solvent evaporation while region III is related with the metalorganic decomposition.

Chemical processes associated to each thermal region as well as the released gases (detected by MS and FTIR) are indicated in Table 3-1.

Stage	T(°C)	Mass loss (%)	Chemical process	Detected gaseous phases	
Ι	r.t70	8.88	Uncoordinated solvents evaporation	Water Methanol Acetone Trifluoroacetic acid	H2O CH3OH CH3COCH3 CF3COOH
II	70-240	18.6	Coordinated solvents thermolysis and evaporation	Methanol Acetone Trifluoroacetic acid Methyl trifluoroacetate	CH3OH CH3COCH3 CF3COOH CF3COOCH3
III	240- 300	38.7	Thermo-oxidative TFA decomposition	Trifluoroacetic acid Trifluoroacetyl fluoride Carbonyl fluoride Carbon dioxide Carbon monoxide	CF3COOH CF3COF COF2 CO2 CO

Table 3-1: Chemical processes and detected gaseous phases associated to each temperature region in TFA

## 3.1.1. Stage I: room temperature up to 70°C

Within this temperature range, the gases detected by MS and FTIR were: water (m/z 18), trifluoroacetic acid (m/z 114, m/z 45, carbonyl absorption band at 1830 cm<sup>-1</sup>), methanol (m/z 29, m/z 31) and acetone (m/z 58, m/z 43) (see Figure 3-2(a) and Table 3-1). The presence of water is due to the high hygroscopic character of trifluoroacetate salts, while the rest of released gases correspond to residual volatile solvents (b.p. <  $73^{\circ}$ C) coming from the synthesis of the trifluoroacetate salts solution.

## 3.1.2. Stage II: 70 °C-240 °C

Methanol, trifluoroacetic acid and acetone were still released within this intermediate thermal region (Figure 3-2(a) and Figure 3-4). Taking into account that the temperature range is higher than the corresponding boiling points of each compound, their detection can be accounted by the thermolysis and consequent evaporation, which indicate that such solvents are coordinated [122]. As an example, in Figure 3-2(a), the acetone molecular ion [CH<sub>3</sub>COCH<sub>3</sub>]<sup>+</sup> is detected at approximately its boiling point (57°C) and it is again observed at temperatures much higher, denoting coordination to a metallic center.



Figure 3-2: Ion mass fragments occurrences of the evolved gases as function of time, measured with TGA-MS for the TFA precursor decomposition in air; a) Acetone molecular ion b) [CF<sub>3</sub>]<sup>+</sup> ion fragment c) Carbon dioxide molecular ion and d) Carbonyl fluoride molecular ion.

It is well known that electron-donor heteroatoms easily coordinate with metallic electronacceptor centers in metal-organic systems. In particular, copper and yttrium complexes coordinated to either methanol or acetone have been already described [123]. Figure 3-3 shows two examples, reported in the literature [124-127], of the molecular structures of Cu and Y carboxylate complexes. Both metals can form dimeric structures in which apart from the carboxylate ligands, other electron-donor molecules (e.g. acetone, methanol, water) are also coordinated due to the avidity of the metallic centers for additional coordination. This is particularly noteworthy in the case of copper (II) trifluoroacetates which their facile reactions with traces of water or any other donor solvent drastically restricted their handling as crystalline "unligated" copper (II) trifluoroacetates [127].

The detection of certain amount of methyl trifluoroacetate (Figure 3-4 (a)), which had not been previously reported, is justified by the reactivity of methanol and trifluoroacetic acid at these temperatures, leading the esterification reaction:  $CF_3COOCH + CH_3OH \rightarrow CF_3COOCH_3 + H_2O$ .



Figure 3-3: Molecular structures of copper and yttrium carboxylates showing additional coordination of electron-donor molecules (X).

## 3.1.3. Stage III: 240°C-300°C

The detection of [CF<sub>3</sub>]<sup>+</sup> and [CO<sub>2</sub>]<sup>+</sup> fragments by MS at the temperature range of 240°C-300°C (Figure 3-2 (b-c)), together with the highest weight loss observed in the TGA (38.7%) are evidence of the thermo-oxidative decomposition of the organic matter. This temperature region was previously identified as that where strong film shrinkage (64% of film thickness) takes place and thus tensile stress relaxation can lead to highly inhomogeneous or even cracked films [104]. For this reason, a tight control of processing parameters within this stage is crucial in order to get homogeneous and smooth films after pyrolysis.

In this stage, the gases evolved during the TFA decomposition were identified as: CF<sub>3</sub>COOH, CF<sub>3</sub>COF, COF<sub>2</sub>, CO<sub>2</sub> and CO (Figure 3-2 (c-d), Figure 3-4 (b)). Further details about their characterization will be given later on.

Here we would like to emphasize that no HF signal was detected via either MS or by FTIR. The same result was previously reported for alkaline earth and rare earth trifluoroacetates conversion into metal fluoride thin films for optical applications [128]. Our results therefore do not support previous, poorly described analysis, which proposed the formation of HF as an exhaust gas in the pyrolysis stage [44,46]. Taking into account that the commonly used electrode for the identification of fluorinated compounds is selective for fluoride ions [129,130], it is very likely that

HF was erroneously identified as a fluoride containing molecule overlooking the presence of other fluorinated gases such as CF<sub>3</sub>COF and COF<sub>2</sub>.



Figure 3-4: FTIR spectra of the released gases detected at different temperatures during TFA precursors decomposition; a) At 195°C the assigned absorption bands correspond to methyl trifluoroacetate, methanol and carbon dioxide and b) Between 272°C and 295°C, to trifluoroacetic acid, trifluoroacetyl fluoride, carbon dioxide and carbon monoxide.

FTIR spectra of the gaseous phases released during TFA decomposition are shown in Figure 3-4 (b). Between 272°C and 295°C, the IR absorption bands at 3580, 1830 and 1200 cm<sup>-1</sup> are assigned to COO—H, C=O, and C—F stretching vibrations which correspond to trifluoroacetic acid (TFAH). On the other hand, no absorption band due to trifluoroacetic anhydride (two intense bands should appear at 1870-1725 cm<sup>-1</sup> due to C=O stretching) has been observed. Trifluoroacetic anhydride (TFAA) easily hydrolyzes to form trifluoroacetic acid, even with moisture from air, thus its atmospheric lifetime is believed to be negligible [131]. Taking into account that the pyrolysis process is carried out in humid atmosphere, it is very likely that TFAH is formed due to TFAA hydrolysis. Nevertheless TFAA was neither detected in dry atmosphere, thus indicating that a certain amount of water must be present in the gas flow. This is consistent with the detection of the water ion mass (m/z 18) at temperatures above  $100^{\circ}$ C (Figure 3-5) as a result of the esterification reaction which takes place within the temperature region II, between 145°C and 240°C.

At higher temperatures (272-295°C) a new absorption band at 1896 cm<sup>-1</sup> appears in the IR spectra (Figure 3-4 (b)) which is assigned to C=O stretching of CF<sub>3</sub>COF[105]. In addition, COF<sub>2</sub>

molecular ion mass was detected by MS within the above-mentioned temperature range (Figure 3-2 (d)).



Figure 3-5: Water ion mass occurrence as a function of time measured with TGA-MS for the TFA precursor decomposition under dry air atmosphere. Water detection at temperatures above 100°C can be justified by its generation in the esterification reaction between methanol and trifluoroacetic acid.

Since TFAH is the first fluorinated compound coming from the decomposition of the trifluoroacetate moiety, we propose that carbonyl fluoride (COF<sub>2</sub>) and trifluoroacetyl fluoride (CF<sub>3</sub>COF) may result from further thermo-oxidative decomposition of TFAH, giving CO<sub>2</sub> and CO as decomposition sub-products. The detection of these fluorinated compounds are in agreement with previous results described in the literature for the decomposition of TFAH and metal trifluoroacetates [128,132].

Although TFAH and HF are both acids (pKa=0.5 and 3 respectively) their toxicity is completely different. HF is physiologically a very powerful chemical since F- ions can bind to Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in the human tissue by simple exposure [133]. In contrast, TFAH is a stable ion in the aqueous phase and no significant F- loss process such as hydrolysis, or photolysis, is identified in air. The other fluorinated compounds detected will be mainly toxic due to the possible formation of HF in their further hydrolysis [134].

As a conclusion, we state that the released gases during the metal-trifluoroacetates precursor decomposition present much lower toxicity than early believed [44,121] since no HF is detected. Moreover, taking into account the high reactivity of HF toward SiO<sub>2</sub>, its absence in the gas exhaust is also advantageous for large scale coated conductors production from a technical viewpoint.

## 3.1.4. Cu Loss due to Cu(TFA)<sub>2</sub> Sublimation

It is well known that the high volatility of copper trifluoroacetate causes its partial sublimation at temperatures above 100°C, thus some processing modifications had been studied to prevent Cu loss. McIntryre *et al.* [39] proposed the addition of water vapour to the gas flow in order to prevent the Cu(TFA)<sup>2</sup> sublimation by its hydro-stabilization. More recently, the addition of diethanolamine (DEA) to the precursor solution provided similar results [43]. However, no detailed study had been accomplished in order to analyze and quantify the process leading to Cu deficiency in the final YBCO superconducting film.

We have studied the Cu(TFA)<sup>2</sup> sublimation through TGA experiments in both dry and humid conditions. When the (Y, Ba, Cu)-TFA precursors were decomposed in dry atmosphere, a solid residue appeared deposited on the tubular furnace tube (Figure 3-6 (a)). The analysis of such residue by inductively coupled plasma confirmed that it contained copper. The amount of Cu(TFA)<sup>2</sup> sublimated has been quantified by the difference of weight loss observed in the TGA curves (Figure 3-6 (b)). In dry air, Cu(TFA)<sup>2</sup> sublimation led to an additional weight loss of ~4% which corresponds to ~9% of Cu deficiency in the final YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> unit formula. Earlier, Dawley *et al.* [135] found that performances of YBCO films, grown under dry conditions, were optimized when an excess of 7.5-9% Cu was added to the precursor solution, which is in agreement with the copper deficiency we have determined.



Figure 3-6: Cu loss due to Cu(TFA)<sup>2</sup> sublimation in dry atmosphere. a) Cu residue deposited on the TGA tubular furnace tube (confirmed by ICP-AES) after pyrolysis in dry air. b) Thermogravimetric analysis of the (Y, Ba, Cu)-TFA precursors showing 4% of additional weight loss in dry conditions.

## 3.2. Influence of the Gas Flow Atmosphere

The role of the oxygen partial pressure is important in coated conductors processing since unfavourable oxidation of the metallic substrate may occur. Moreover, the oxidizing power of the gas flow during pyrolysis may affect the thermo-oxidative decomposition kinetics as well as the solid deposit composition. In this section we present the influence of the gas flow atmosphere in the composition of the intermediate solid phases as well as in the surface morphology and porosity of the as-decomposed films.

# 3.2.1. Intermediate Solid Phases of the As-Decomposed Films

Previous TEM studies determined that oxygen-decomposed films were a mixture of amorphous regions, intermediate nanocrystalline phases and porosity [52]. Two-dimensional XRD of decomposed films proves the polycrystalline nature of the intermediate phases (Figure 3-7), which in oxygen atmosphere have been identified as CuO and Ba<sub>0.72</sub> Y<sub>0.28</sub>F<sub>2.28</sub> (BYF) solid solution [38,52]. However, we note that the intensity of the CuO (111)+(200) Bragg peaks is not uniformly distributed along the diffraction ring denoting some preferred orientation of the nanocrystallites. The Y content in the fluoride solid solution was determined from the measured lattice parameter, following a procedure previously reported [136].



Figure 3-7: Two-dimensional XRD pattern of a pyrolyzed 500nm-thick film under standard heating conditions and flow oxygen gas atmosphere. Diffraction cones show the polycrystalline nature of the resultant phases after decomposition, even though some preferred orientation is observed for CuO. Spots come from the single-crystal LaAlO3 substrate.

Although BYF crystallizes independently of the oxygen partial pressure, the Cu oxidation state in the oxide phase is strongly affected. A highly oxidizing atmosphere accelerates the thermo-oxidative decomposition reaction leading to copper (II) oxide, while the reduced form (Cu<sub>2</sub>O) was obtained in inert N<sub>2</sub> atmosphere. Finally, a mixture of both copper oxide phases was observed in air (Figure 3-8 (a)). Additionally, the FTIR analysis of the evolution of the carboxylate group indicates that TFA decomposition is slowed down at reduced oxygen partial pressures (Figure 3-8(b)). The reaction times needed for the complete TFA decomposition are: 50 min in N<sub>2</sub>, 35 min in air and 15 min in O<sub>2</sub>



Figure 3-8: a) X-Ray diffraction patterns of films pyrolyzed in N<sub>2</sub>, air and O<sub>2</sub>. b) FTIR analysis of the carboxylate evolution with time during pyrolysis under different atmospheres. The reaction times needed for the complete TFA decomposition are: 50 min in N<sub>2</sub>, 35 min in air and 15 min in O<sub>2</sub>.

To conclude and considering the results of the gaseous' and solid phases' analysis in air atmosphere, we propose the following chemical reaction for the decomposition of the TFA precursor salts:  $Y(CF_{3}COO)_{3}(s) + 2Ba(CF_{3}COO)_{2}(s) + 3Cu(CF_{3}COO)_{2}(s) \xrightarrow{air} \\ YF_{3}(s) + 2BaF_{2}(s) + (3-y)CuO(s) + y/2Cu_{2}O + 6CF_{3}COF(g) + 4COF_{2}(g) + (3-y/2)CO_{2}(g) + (7+y/2)CO(g) \\ BaF_{2} + xYF_{3} \xrightarrow{air} Ba_{1-x}Y_{x}F_{2+x}$ 

## Scheme 3-3: Decomposition chemical reaction of the metal-trifluoroacetates in air.

The *y* coefficient in Scheme 3-3 is related to the Cu<sub>2</sub>O fraction formed by reducing oxygen partial pressure in the gas flow. An increase of CO (y/2 mol) is related with the equivalent formation of Cu<sub>2</sub>O which is a metastable phase in air at this temperature. Therefore, it is very likely that the proposed decomposition reaction (Scheme 3-3) is valid either in inert, reducing or oxidizing atmospheres if we take into account that the CuO/Cu<sub>2</sub>O ratio is modified with PO<sub>2</sub>.

#### 3.2.2. Surface Morphology and Porosity Development is As-Decomposed Films

A general feature of the chemically-derived films is that a large fraction of precursor volume is eliminated during pyrolysis, hence leading highly porous films [24,25]. Therefore, porosity has been essentially related to film shrinkage. Moreover, blistering and internal stress relaxation may strongly affect the integrity of the thin film which can have detrimental effects in the further film crystallization. It has been recently studied in our group [104] that through control of several processing parameters during TFA pyrolysis (temperature, gas flow and heating rate) the stress relief smoothed and homogeneous pyrolyzed films could be achieved.

However, the high degree of porosity is still an issue that up to now remains unsolved. Residual pores in YBCO films are undesirable because they behave as current blocking defects thus decreasing the percolating critical current density (J<sub>c</sub>) [137,138]. Feenstra *et al.* [139] proposed a densification step based in an intermediate high temperature annealing. However, this process was accompanied by the formation of a liquid phase which has detrimental effects from the viewpoint of compositional and structural control.

We have analyzed the decomposed films through Scanning Electron Microscopy (SEM) and Focused Ion Beam (FIB) in order to assess whether the different decomposition paths have an influence on the porosity and surface morphology. Figure 3-9 displays SEM images of as-decomposed films in pure oxygen (P<sub>Total</sub>=1atm), air (Po<sub>2</sub>=0.2atm, P<sub>N2</sub>=0.8atm) and pure nitrogen (P<sub>Total</sub>=1atm). As opposed to the high homogeneity of the oxygen-pyrolyzed films (Figure 3-9 (a)),

decomposition in air and nitrogen (Figure 3-9 (b,c)) led to inhomogeneous surfaces associated with the presence of Cu<sub>2</sub>O microparticles, as confirmed by X-ray Energy Dispersive Spectroscopy (EDX) and in agreement with XRD (Figure 3-8 (a)).



Figure 3-9: SEM images of as-decomposed films: (a) in oxygen, (b) air and (c) nitrogen gas flow

Nevertheless, the presence of Cu<sub>2</sub>O microparticles at the film surface of the pyrolyzed films was accompanied by a strong decrease of porosity as it can be observed in Figure 3-10. FIB crosssection image of a standard-oxygen-pyrolyzed film (Figure 3-10(a)) evidences the formation of vertical open porosity which, due to its morphology and taking into account the poor mechanical properties of the films at this stage [34], we attribute to a fast gas escape towards the film surface. Through image analysis (Mountains software) we have estimated that oxygen-pyrolyzed films exhibit ~30% porosity. We would like to underline that the observed pores are not the commonly featured by chemically-derived films in which shrinkage is the main source of porosity [25]. In our case, the vertical morphology of the pores leaves no room for doubt that the gas escape plays an important role in the formation of such pores. Therefore, we believe that porosity may be reduced by lowering the decomposition kinetics, i.e. lowering the pyrolysis temperature. Accordingly, porosity was reduced down to ~15%, in samples pyrolyzed at 275°C instead of at 310°C (Figure 3-10 (d)). In addition, the high exothermicity typical of thermo-oxidative decompositions also plays an important role in the porosity generation since the reaction results in a thermal runway (selfheating) accelerating the gas release towards the surface. Consequently, when the decomposition was carried out in less oxidizing atmospheres (i.e. low oxygen partial pressure), porosity decreased down to  $\sim 5\%$  in air, becoming negligible in N<sub>2</sub> (Figure 3-10(b-c)). We associate this observation to the fact that the enthalpy change becomes less negative, being even positive under inert atmospheres [140,141].

We conclude that porosity in pyrolyzed films can be accurately controlled by changing the decomposition reaction path, which depends on an intricate contribution of thermodynamic and kinetic factors determining the slow decomposition rate (gas escape rate) and the occurrence of a self-heating effect. Another relevant aspect of this study is that porosity does not depend on the gas exhaust composition. Dense films with no blistering or bubbling are obtained with no need of

reducing the fluorine content from the metal-organic precursors as proposed by some authors [44,118].



Figure 3-10: FIB images of pyrolyzed films processed at 310°C in (a) pure oxygen (b) air (c) pure nitrogen and d) at 275°C under pure oxygen atmosphere

We have demonstrated that porosity is strongly reduced under less oxidizing atmospheres, however then undesirable Cu<sub>2</sub>O coarsening and further exo-diffusion to the film surface was observed (Figure 3-11(a,b)). The lower decomposition temperature of Cu(TFA)<sub>2</sub> with respect to the other salts<sup>1</sup> as well as slower decomposition when Po<sub>2</sub> is reduced (Figure 3-8 (b)) seems to be the reason for the Cu<sub>2</sub>O ripening [41].

As mentioned before, non-porous YBCO films are desired because pores behave as current blocking defects thus decreasing J<sub>c</sub>. However, it is not possible at the present stage to quantitatively correlate the low porosity of films pyrolyzed in air and N<sub>2</sub> with the observed J<sub>c</sub> values because a full investigation of the influence of YBCO growth conditions on the final microstructure in both cases should be carried out. This study is out of the scope of the present work, however, the typical

<sup>&</sup>lt;sup>1</sup> The decomposition temperature of each trifluoroacetate salt has been investigated by TGA in air atmosphere: T~225 °C for Cu(TFA)<sub>2</sub> and T~275-305 °C for Y(TFA)<sub>3</sub> and Ba(TFA)<sub>2</sub>

J<sub>c</sub> values of films pyrolyzed at low oxygen pressures and grown under standard conditions [34,54] were in the range of 2-3 MAcm<sup>-2</sup> at 77 K, thus denoting that films with high quality can also be achieved under these pyrolysis conditions. Further investigation is required in order to optimize the growth process of TFA-YBCO films pyrolyzed at low oxygen pressures.



Figure 3-11: FIB cross-sectional images showing both Cu<sub>2</sub>O coarsening and porosity reduction in pyrolyzed films processed in (a) air and (b) nitrogen atmosphere. (c) Unidentified particles in as-grown YBCO film (from N<sub>2</sub>-pyrolysis).

# 3.3. Conclusions

The identification of the released gases during the metal-trifluoroacetate thermal decomposition in air has allowed us to determine the complete decomposition reaction, which moreover is valid at different atmospheres by varying the CO/CO<sub>2</sub> ratio in the released gases and the CuO/Cu<sub>2</sub>O ratio in the solid product. Although the presence of HF in the gaseous phases was widely established, HF was not detected in the present study. Instead, CF<sub>3</sub>COOH, CF<sub>3</sub>COF and COF<sub>2</sub>, were released as fluorinated compounds. It is noteworthy that the absence of HF in the gas exhaust is advantageous for large scale coated conductors production from both technical (reactivity with SiO<sub>2</sub>) and toxicity viewpoints.

Films pyrolyzed in a highly oxidizing atmosphere such as pure oxygen showed strong vertical porosity due to the fast thermo-oxidative decomposition kinetics together with a thermal runway effect. Therefore, in order to avoid the formation of such pores, which are undesirable for the final superconducting performances, an accurate control of both thermodynamic and kinetic effects of the decomposition reaction is needed. However, we have found new process conditions to eliminate the porosity in these materials. The gas exhaust rate is a key factor to control the residual porosity being strongly reduced by lowering the gas flow oxygen partial pressure (e.g. air atmosphere). Accordingly, dense films were obtained after TFA decomposition in inert atmosphere (e.g. nitrogen) due to the contribution of both lower decomposition kinetics and the endothermic nature of the reaction. In that case, however, Cu<sub>2</sub>O coarsening and consequent phase segregation in the final YBCO superconducting film was observed.

Finally, we state that fine tuning of the pyrolysis process may be achieved to keep an optimal microstructure and homogeneity of the pyrolyzed films at high decomposition rates.

# 4. Nucleation and Final Structure of YBCO Nanocomposite Films

Achieving an efficient and viable superconducting film requires a fine balance between defects at both the nanoscale and mesoscale level. As stated in the introduction, both YBCO lattice defects and non-superconducting nanostructures can effectively pin the magnetic flux, thus enabling high J<sub>c</sub> in external applied magnetic fields. However, at the mesoscopic scale, J<sub>c</sub> depends on the homogeneity of the grain-to-grain connectivity because supercurrents must percolate along the whole sample. Therefore, high quality of biaxial crystallographic alignment of the superconducting YBCO domains is required. Paradoxically then, the trick is to achieve a single crystal-like YBCO layer featuring imperfections at the nanoscale level.

Barium perovskite nanoinclusions BaBO<sub>3</sub> (B =Zr, Hf, Sn) [9,62,78] and binary rare earth oxides RE<sub>2</sub>O<sub>3</sub> (RE= Y, Dy, Ho) [79,82,142] have been successfully incorporated to YBCO epitaxial matrix by different deposition techniques leading to nanocomposite films with improved flux pinning properties. Nevertheless, one must take into account that the embedded nanostructures reduce the current-carrying cross section. Therefore an optimum volume fraction of nanoparticles exist, in which the increase of J<sub>c</sub> due to vortex pinning dominates over the decrease associated to the reduced percolation path (current-blocking effects). Moreover, the density, distribution and separation between the pinning centers are also crucial issues regarding the competition between pinning and current-blocking. This issue was treated within a theoretic framework by Gurevich *et* 

*al.* [143] who found that ~10 % volume fraction of insulating nanoinclusions was the trade-off value. This value was calculated considering nanoparticles of radius (r<sub>0</sub>) ranging from  $\xi$  to 3 $\xi$  and nanoparticle's spacing between 3.4r<sub>0</sub> and 3.8r<sub>0</sub>. Moreover, the presence of a secondary phase can have influence on the YBCO texture and/or its mosaic spread thus affecting the superconducting properties.

For all the reasons above mentioned and taking into account that solution-derived YBCO nanocomposites (NCs) were still not reported at the beginning of this thesis, it happen to be of great importance to well characterize them from a structural viewpoint. Moreover, understanding the influence of the nanoinclusions on the YBCO texture is essential to further correlate structure and superconducting properties.

It has been already mentioned in the introduction that the firsts YBCO NCs were achieved through *in situ* deposition techniques such as PLD, by using mixed targets (YBCO + inclusion phase)[9,60,80]. Because of the non-equilibrium nature of the <sup>PLD</sup>film growth process, the surface diffusion of adatoms is high enough to allow the heteroepitaxial growth of the nanoinclusions leading to coherent or semicoherent interfaces. Therefore, nanoinclusions incorporated in <sup>PLD</sup>YBCO NCs always sustain a specific crystallographic orientation relationship with YBCO. Consequently, and if the atomic mobility of the adatoms is high enough, the formation of self-assembled nanostructures (nanorods) occur due to minimization of mismatch strain. Therefore, lattice mismatch between YBCO and the inclusion become a key parameter to control the formation of either homogeneously distributed nanoparticles or self-aligned nanorods in <sup>PLD</sup>YBCO NCs. Besides, the deposition rate controls also the growth rate of the nanocomposite.

On the contrary, a different scenario may emerge in *ex situ* solution-based YBCO-NC (<sup>MOD</sup>YBCO-NC) as the growth process completely differs from PLD. Indeed, the nanostructuring landscape may drastically change in <sup>MOD</sup>YBCO-NC owing to the fact that growth process is closer to equilibrium with volume diffusion of mobile species (happening after deposition) rather than surface diffusion. It is then feasible that the nanoinclusions do not perforce sustain an epitaxial relationship with YBCO leading to incoherent interfaces which up to now have been very little studied.

In this chapter, we present a detailed structural characterization by XRD and TEM of YBCO-Y<sub>2</sub>O<sub>3</sub> and YBCO-BaZrO<sub>3</sub> NCs films grown by CSD-MOD. We have chosen BaZrO<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> as secondary phases because of their compatibility with YBCO and because they already have given promising results when added to YBCO via *in situ* techniques. In addition the dissimilar structures and lattice parameters of BaZrO<sub>3</sub> (cubic perovskite, a= 4,188Å) and Y<sub>2</sub>O<sub>3</sub> (cubic bixbyite,

a= 10,602Å) will likely imply different misfit lattice strain in the nanocomposites. In Figure 4-1 are represented the unit cells of YBCO,  $Y_2O_3$  and  $BaZrO_3$ .



Figure 4-1: Solid spheres model of the unit cells of a) YBCO, b) Y<sub>2</sub>O<sub>3</sub> and c) BaZrO<sub>3</sub> Y atoms are represented as yellow spheres, Cu in blue, Ba in light purple, Zr in dark purple and O in dark green.

Misfit lattice strain is an important parameter in epitaxial systems. The term epitaxy is commonly used in thin films and refers to the growth of a single-crystal layer on top of a single-crystal substrate in a way that the periodicity of the atoms on the substrate surface is the template for the epitaxial growth of the film. But the term epitaxy (or strictly heteroepitaxy due to dissimilar materials involved) is also used in other systems rather than thin films. Any interfacial system in which the two phases hold a common crystallographic structure is denominated epitaxial. A practical way to denote an epitaxial relationship is using the Miller indices, that is, specifying the normal to a plane (*hkl*) and a direction contained in that plane [*hkl*]. Epitaxial relationships can be generally predicted on the basis of lattice misfit arguments. Those planes and directions which give the best fit often determine the orientation of the interfacial system. Therefore, considering the differences in the interplanar distances of both structures, it is defined the so-called lattice misfit ( $\delta$ ), as:  $\delta = (d_s - d_f)/d_f$ , where  $d_s$  and  $d_f$  are the interplanar distances of the substrate (or phase 1) and film (or phase 2) respectively.

Lattice parameters and distances of matching (*dofm*) corresponding to the substrates and oxide nanostructures used through this work are shown in Table 4-1. NCs films were grown indistinctly on (001)-oriented SrTiO<sub>3</sub> and (001)-oriented LaAlO<sub>3</sub> (considering pseudocubic structure for the latter). LaAlO<sub>3</sub> (LAO) has a rhombohedral (r) structure, however, it is often considered as pseudocubic (pc) because the cell parameter of the rhombohedral structure,  $a_r=5.364$  Å, corresponds to the direction <110> of the cubic structure. Then the cubic cell parameter will be given by  $a_c=a_r/\sqrt{2}$  (i.e. 3.79 Å). It is noteworthy to mention that at high temperature, LAO exhibits a perovskite-type simple cubic structure; and at T<sub>c</sub>~500°C undergoes a phase transition to the

distorted perovskite rhombohedral structure. As consequence of this transition, a twin domain structure develops to relieve strain when LAO is cooled below the critical temperature.

Generally, in the field of thin films, only the in-plane lattice mismatch with the substrate is taken into account. However, in nanocomposite films, the out-of-plane mismatch must be also considered due to the presence of the 3D-nanoparticles. In fact, it has been recently reported [4] that the out-of-plane matching (also called vertical matching) is the one dominating the overall strain state in complex oxide nanocomposites films containing embedded self-assembled nanorods. So, in Table 4-1 is also given the out-of-plane lattice mismatch to YBCO for both substrates and nanoparticles.

Table 4-1: Summary of lattice parameters and distances of matching (*dofm*) of the substrates and oxide nanostructures used. The corresponding mismatch to YBCO is also given.

Material	Crystal System / Stucture Parameter (Å)	ao, Lattice	Distance of Matching,	Mismatch to YBCO <sup>ii</sup> (%)		
		dofm (Å)	a	b	c/3	
LaAlO3 (substrate)	pseudocubic / perovskite	3.792	3.792	-0.81	-2.42	-2.64
SrTiO₃ (substrate)	cubic / perovskite	3.905	3.905	2.14	0.49	0.27
BaZrO₃ (inclusion)	cubic / perovskite	4.188	4.188	9.55	7.77	7,53
Y2O3 (inclusion)	cubic / bixbyite (Mn2O3)	10.602	$10.6\sqrt{2/4} = 3.749$	-1.94	-3.53	-3.74

<sup>ii</sup> Mismatch (%) = 100 x ( $dofm_{material} - a_{0YBCO}$ )/  $a_{0YBCO}$ ; where YBCO lattice parameters are: a= 3,823 Å, b=3,886 Å and c=11.684 (c/3= 3.895 Å).

The concentration of nanoparticles tested was within the range of 4-25 mol% and the equivalent volume fraction is listed in the Table 4-2.

Typical film thicknesses were found to be in the range of 220-270 nm (determined from profilometry measurements and cross-sectional SEM and TEM images). Although thicker NCs films (600-800nm) have been also achieved in the group through multilayering and/or by modification of the deposition parameters, we solely focus on thinner films as a model system.

Besides the basic phase-structural analysis of the NCs, it will be also depicted in this chapter, the nucleation process of the nanoparticles and the influence of their concentration on the texture of YBCO.

(14,10())	(Volume %)		
(MOI %)	BaZrO <sub>3</sub>	Y2O3	
5	2,19	2,21	
10	4,5	4,56	
15	6,98	7,05	
20	9,61	9,71	
25	12,4	12,5	
30	15,42	15,56	

## Table 4-2: Nanoparticle's content in nanocomposite films

# 4.1. Nucleation of Nanoparticles in the Nanocomposites: Quench Experiments

In solution-based nanocomposites, the growth mechanisms of the nanoinclusions strongly influence on their crystallographic orientation thus affecting the interfacial energy. Both preferred and randomly oriented nanoparticles can be achieved depending on their nucleation temperature respect to that of the film. This versatility, inherent of the *ex situ* growth methods, cannot be reached with *in situ* growth techniques in which only fully heteroepitaxial nanostructures have been obtained.

In this section, the results obtained through XRD and TEM analysis of nanocomposites quenched from growth temperature to room temperature will be described in terms of nucleation mechanisms of the nanoparticles within the film matrix. The aim of quenching is to stop (freeze) the reaction evolution of the precursor film by a rapid cooling of the sample, i.e. removing the sample from the furnace.

# 4.1.1. Y<sub>2</sub>O<sub>3</sub> Nucleation

The two-dimensional XRD pattern of a YBCO- Y<sub>2</sub>O<sub>3</sub> nanocomposite quenched from 810°C at t=0min (Figure 4-2(a)) evidences the expected intermediate phases (BaF<sub>2</sub>, Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> (Y225), CuO)) at this initial stage of the YBCO precursor evolution [52]. The diffraction rings denote the polycrystalline nature of the intermediate phases. Moreover the presence of diffraction spots at  $2\theta$ ~30.5° ((004) <sup>YBCO</sup>) and  $2\theta$ ~38.4° ((005) <sup>YBCO</sup>) indicate that *c*-oriented YBCO grains have already started to nucleate. While time increases (t=5min), the YBCO heteroepitaxial growth befalls at expenses of the polycrystalline intermediate phases. It is in this stage when the Y<sub>2</sub>O<sub>3</sub> phase starts to be detected by XRD (Figure 4-2(b)). Assuredly Y<sub>2</sub>O<sub>3</sub> nucleates concurrently with YBCO at the front

growth due to the excess of Y in the precursor matrix. Figure 4-2 (b) displays the 1D-XRD pattern resulted from the chi-integration of the 2D-XRD in which it is noticeably that Y<sub>2</sub>O<sub>3</sub> nucleation is concomitant to YBCO growth. The presence of a single diffraction spot at  $2\theta$ -34° ((004) reflection of Y<sub>2</sub>O<sub>3</sub>) evidences a preferred *c*-orientation of the Nps. However, a diffraction ring at  $2\theta$ -29° ((222) reflection of Y<sub>2</sub>O<sub>3</sub>) is observed in the sample quenched after 10 min at the growth temperature signalling that a certain Y<sub>2</sub>O<sub>3</sub> fraction remains at last randomly oriented. TEM studies are under way, which probably will give an explanation of the presence of the randomly oriented Y<sub>2</sub>O<sub>3</sub> content of 10 mol%, as it will be discussed in Chapter 5, section 5.2.1) which supports the hypothesis that Y<sub>2</sub>O<sub>3</sub> nucleates mainly at the epitaxial YBCO front growth leading to essentially oriented Y<sub>2</sub>O<sub>3</sub> Nps.



Figure 4-2: XRD patterns of YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposite films (20 mol. % Y<sub>2</sub>O<sub>3</sub>) quenched from growth temperature (810°C) at different times (0, 5, 10 min). a) 2D-DRX patterns showing the evolution of the polycrystalline intermediate phases towards the heteroepitaxial YBCO growth. b) Chi-integrated XRD pattern evidencing the presence of the Y<sub>2</sub>O<sub>3</sub> phase.

Nevertheless, a different scenario is displayed by YBCO-BZO nanocomposites as it will be discussed next.

# 4.1.2. BaZrO<sub>3</sub> Nucleation

Unlike YBCO-Y<sub>2</sub>O<sub>3</sub>, the BZO phase  $(2\theta \sim 30^{\circ} \text{ and } 2\theta \sim 42.8^{\circ})$  is present in the nanocomposite at t=0min (810°C) (Figure 4-3) indicating that the nucleation of the BZO nanoparticles occurs prior to the complete YBCO heteroepitaxial growth. TEM studies also confirmed this result.



Figure 4-3: X-ray diffraction patterns of an YBCO-BZO nanocomposite (10 mol % BZO) quenched from its growth temperature (810°C at 0 min): a) 2D-XRD pattern (y-axis represents the  $\chi$  angle) showing the polycrystalline nature of the precursor matrix; b) Chi-integrated XRD pattern evidencing the presence of the BZO phase.

The cross section TEM image in Figure 4-4(a) presents important features. On the one hand, BZO nanoparticles appear perfectly crystallized within the precursor oxy-fluoride matrix and coexisting with the typical polycrystalline segregated phases (CuO and Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>). On the other hand, the substrate interface features a 6 unit cell height YBCO layer in which BZO Nps are also localized. Thus, the presence of BZO when the growing YBCO layer is only 7nm height confirms that BZO nanoparticles have been nucleated previously to the heteroepitaxial YBCO film growth. Moreover, the (001)-oriented SrTiO<sub>3</sub> single-crystal substrate induce the [001]-orientation (~9% inplane mismatch) of those BZO Nps nucleated heterogeneously at the substrate interface. Therefore interfacial BZO Nps present a cube-on-cube epitaxial relationship with the substrate and at the same time with the perovskite sub-cells of the YBCO lattice. On the contrary, these BZO nanoinclusions homogeneously nucleated within the precursor matrix do not sustain any specific orientation relationship with the surrounding oxy-fluoride. In fact, it is very likely that the poor crystallinity of the oxy-fluoride as well as the polycrystalline nature of the intermediate phases is responsible for the random orientation of the bulky BZO Nps.



Figure 4-4: Cross section TEM images of an YBCO-BZO nanocomposite quenched from its growth temperature (810°C at 0 min). a) BZO nanoparticles embedded in the precursor matrix (circle) and growing YBCO layer of few nanometers height (rectangle); b) High resolution TEM image of a bulk BZO nanoparticle, along with its corresponding FFT spectrum as inset and c) High resolution TEM image of the substrate-precursor interface which features a 6 unit cell height YBCO layer with an embedded interfacial BZO nanoparticle.

# 4.2. Basic Structural Characterization of the Resultant Nanocomposites

This section describes the phase-structural characterization of the fully grown nanocomposites through XRD, TEM and SEM analysis. The influence of the concentration of nanoinclusions in the YBCO texture quality and surface morphology is also discussed.

# 4.2.1. Phase Analysis of YBCO-Y<sub>2</sub>O<sub>3</sub> Nanocomposite Films

2D-XRD pattern of a completely grown YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposite evidences that the intermediate phases have fully reacted to the expected YBCO and Y<sub>2</sub>O<sub>3</sub>, both exhibiting a high degree of *c*-axis alignment since (00l) single spots for the orthorhombic YBCO and the (400) spot of the cubic Y<sub>2</sub>O<sub>3</sub> are present (Figure 4-5). However, a randomly oriented fraction of Y<sub>2</sub>O<sub>3</sub> is also present in the nanocomposite as evidences the diffraction ring located at  $2\theta$ -29° which correspond to the most intense reflection for cubic Y<sub>2</sub>O<sub>3</sub> (222). Y<sub>2</sub>O<sub>3</sub> crystallizes in the cubic bixbyite structure in the space group Ia-3.



Figure 4-5: XRD pattern (2D detector) of a fully grown YBCO-Y $_2O_3$  (10 mol.% Y $_2O_3$ ) nanocomposite film on a LAO substrate

Due to the low resolution (~0.04°) of the 2D-diffractometer, the determination of *d*-spacings has been performed with a conventional 0D (point) detector which is preferable for such purpose. The measurements have been performed at two different 2 $\theta$  ranges (Figure 4-6) in order to get enough Y<sub>2</sub>O<sub>3</sub> intensity (better statistics) and at the same time avoid the intense signal of the singlecrystal substrate which can cause saturation in the detector. It is worth mentioning that the (222) line of Y<sub>2</sub>O<sub>3</sub> is missing in the conventional XRD pattern due to the fact that the measurement is confined within a plane (diffractometer plane). The point detector makes 2 $\theta$  scan along a detection circle and consequently the diffraction data out of the diffractometer plane are not detected. On the contrary with a 2D detector, the measurable diffraction is no longer limited in the diffractometer plane and a large portion of the diffraction ring can be measured simultaneously.



Figure 4-6: Conventional XRD diffraction patterns (0D detector) of a fully grown YBCO-Y<sub>2</sub>O<sub>3</sub> (10 mol% Y<sub>2</sub>O<sub>3</sub>) nanocomposite film on a LAO substrate.

The *c* lattice parameters of YBCO and Y<sub>2</sub>O<sub>3</sub> do not significantly vary in the whole range of Y<sub>2</sub>O<sub>3</sub> concentration investigated (10-20 mol %). They have been determined by a profile fitting procedure using all the (*001*)-YBCO lines and the (400)-Y<sub>2</sub>O<sub>3</sub> line. The mean lattice parameters and the correspondent standard deviation are represented in Table 4-3 along with the expected bulk values. The results reveal a slightly difference in the cubic Y<sub>2</sub>O<sub>3</sub> lattice parameter. Normally, such small differences in cell parameters can be accounted for macrostrain or formation of a solid solution where Y<sup>3+</sup> have been substituted by another cation with similar ionic radii ((RE<sub>1-x</sub>Y<sub>x</sub>)<sub>2</sub>O<sub>3</sub>, RE: Ho, Gd, Tm, Eu,Yb, Sm) [144].

Table 4-3: *c* lattice parameters of orthorhombic YBCO and cubic Y<sub>2</sub>O<sub>3</sub> phases in the YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposites (10-20 mol.% Y<sub>2</sub>O<sub>3</sub>) determined from the measured d-spacings and compared with the bulk values. The standard deviation between parentheses accounts for the last decimal.

Phase	Bulk <i>c</i> lattice parameter (Å)	<i>c</i> lattice parameter in the nanocomposite film (Å)
YBCO	11.684	11.685 (3)
Y <sub>2</sub> O <sub>3</sub>	10.602	10.580 (2)

However the observed difference in Y<sub>2</sub>O<sub>3</sub> lattice parameter cannot be explained either in terms of macrostrain since Y<sub>2</sub>O<sub>3</sub> should undergo a tensile strain in order to match with *c* lattice parameter of YBCO. Neither, obviously, in of terms rare earth (RE) substitution. Considering that the *d*-spacing determination has been performed only with one Y<sub>2</sub>O<sub>3</sub> line ((400) at  $2\theta$ =33.9°) and the worse resolution at low  $2\theta$  values, it is thus very likely that such variation could be purely associated with the experimental error.

Y<sub>2</sub>O<sub>3</sub> domain sizes (along *c*-axis direction) have been estimated from the integral breadth of the (400) line of Y<sub>2</sub>O<sub>3</sub> by using the Scherrer formula,  $D=0.9\lambda/(\beta\cos\theta$  [99]. This expression relates the integral breadth ( $\beta$ ) of the peak in a 2 $\theta$ -scan with the apparent domain size along the diffracting plane normal. In order to not overestimate the results, the instrumental broadening has been subtracted. An average size of 27 (2) nm for all concentration range (10-20 mol.% Y<sub>2</sub>O<sub>3</sub>) has been obtained indicating that no coarsening exist (growth of some Nps at expenses of others which shrink). Besides, TEM studies in YBCO-Y<sub>2</sub>O<sub>3</sub> (with 30 mol% Y<sub>2</sub>O<sub>3</sub>) do not show any sign of Np coalescence (two Np touch each other). Instead, isolated and homogeneously distributed Nps located either at the substrate interface (interfacial Y<sub>2</sub>O<sub>3</sub>) or within the bulk of the film (bulky Y<sub>2</sub>O<sub>3</sub>) have been detected by TEM with sizes ranging 10-30 nm (Figure 4-7). TEM analysis demonstrate that Y<sub>2</sub>O<sub>3</sub> nanoinclusions are single-crystalline showing either an epitaxial relationship or not with the surrounding YBCO matrix. Interfacial Y<sub>2</sub>O<sub>3</sub> nanocrystals (Figure 4-7(a)) are always epitaxial due to the heterogeneous nucleation at the substrate interface which induces the epitaxial growth of the nanoparticles. By contrast, the Y<sub>2</sub>O<sub>3</sub> Nps located within the bulk of the YBCO matrix, are found to be epitaxial (Figure 4-7(b)) or randomly oriented (Figure 4-7(c)) in agreement with 2D-DRX results. As discussed before, quench experiments indicated that Y<sub>2</sub>O<sub>3</sub> nucleate concomitantly with YBCO at the growth front. However, the additional presence of randomly oriented nanoparticles point that some fraction of Y<sub>2</sub>O<sub>3</sub> nucleates also homogeneously within the amorphous precursor matrix, prior the YBCO growth front traps them. It is remarkable that those randomly oriented nanoparticles display spherical morphology which indicates that the interfacial energy is isotropic. By contrast, epitaxial nanoparticles appear facetted and with disk morphologies in agreement with the low lattice mismatch with both the YBCO matrix and the substrate.

Regarding the epitaxial Nps, they hold a single crystallographic orientation relationship with YBCO:  $(001)[110]Y_2O_3//(001)[100]YBCO$ , i.e.  $(001)-Y_2O_3$  crystallographic planes parallel to (001)-YBCO ones and the [110] direction of Y2O<sub>3</sub> parallel to the [100] direction of YBCO, that is Y2O<sub>3</sub> unit cell is 45° in plane rotated.



Figure 4-7: High resolution TEM images of Y<sub>2</sub>O<sub>3</sub> nanoparticles in YBCO- Y<sub>2</sub>O<sub>3</sub> (30 mol %) nucleated a) at the substrate interface and b,c) at the bulk of the YBCO film. Nanoparticles in a) and b) are epitaxial while the one showed in c) remains randomly oriented.

# 4.2.2. Phase Analysis of YBCO-BaZrO<sub>3</sub> Nanocomposite Films

Like YBCO-Y<sub>2</sub>O<sub>3</sub>, YBCO-BZO nanocomposite films feature the expected phases with *c*preferred orientation i.e. *c*-axis oriented perpendicular to the substrate surface as is seen from the solely presence of (00*l*) diffraction spots in the 2D-diffraction pattern (Figure 4-8). Additionally a randomly oriented BZO fraction is present as evidenced for the diffraction ring at  $2\theta$ ~30° which accounts for the (110)-BZO maximum intense line. BZO crystallizes in the cubic perovskite structure in the space group Pm-3m. It is remarkable that no secondary phases or impurities are observed, which denotes that BZO precursor salts have completely reacted and crystallized to form the BZO phase under the standard YBCO growth conditions.



Figure 4-8: XRD pattern (2D detector) of a fully grown YBCO-BZO (10 mol% BZO) nanocomposite film on a LAO substrate.

Out-of-plane cell parameters of YBCO and BZO have been determined from conventional XRD (Figure 4-9) through a profile fitting procedure. They remain constant for the whole range of BZO concentration investigated (4-20 mol% BZO). Table 4-4 shows the mean values of the lattice parameters obtained for the YBCO-BZO nanocomposite films along with the expected bulk values. The standard deviation accounts for the dispersion between samples with different BZO content, not for the fitting error.



Figure 4-9: Conventional XRD diffraction patterns (0D detector) of a fully grown YBCO-BZO (10 mol.% BZO) nanocomposite film on STO substrate.

While YBCO c lattice parameter keeps unaffected, BZO cubic cell parameter in the nanocomposites (4,227 Å) shows a significant variation with respect to the bulk value (4,188 Å). It

is well-known that Y-doped BZO causes the enlargement of the perovskite cell owing to a  $Zr^{4+}$  substitution by Y<sup>3+</sup> (BaZr<sub>1-x</sub>Y<sub>x</sub>O<sub>(3-x/2)</sub>) which has bigger ionic radius [145,146]. Schober et al. [145]., found a linear dependence of the cell parameter of the solid solution on the substitution parameter x. Taking into account such variation, our estimated lattice parameter of 4.227 Å corresponds to x=0.2 meaning that 20% of Zr<sup>4+</sup> has been substituted by Y<sup>3+</sup> in the BZO nanoparticles. This composition is in agreement with solution-based Y-doped BZO films (BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>2.9</sub>), earlier reported [147]. For simplicity, we will keep designating BaZrO<sub>3</sub> in spite of the Y-Zr substitution.

Table 4-4: *c* lattice parameters of orthorhombic YBCO and cubic BZO in the YBCO-BZO nanocomposites (4-20 mol.% BZO) determined from the measured d-spacings and compared with the bulk values. The value in parenthesis stands for the standard deviation.

Phase	Bulk <i>c</i> lattice parameter (Å)	<i>c</i> lattice parameter in the nanocomposite films (Å)
YBCO	11,684	11,686 (3)
BaZrO <sub>3</sub>	4,1880	4,227 (4)

The occurrence of such Zr-Y substitution in BZO is of extremely importance because it triggers an Y-deficiency in the final stoichiometry of the TFA precursor solution, being more significant at high BZO concentrations. In fact, the main detrimental effect observed of Y-deficiency was a considerable reduction of the YBCO critical temperature (T<sub>c</sub>) which was found to be in the range of ~86-88K (estimated from temperature dependence magnetization measurements). By adding an equivalent excess of Y(TFA)<sub>3</sub> salt to the initial solution, the non-stoichiometry was compensated and consequently the resulting T<sub>c</sub> values were the expected ones (~91K) as shown in Figure 4-10. It bears mentioning that, other sources of T<sub>c</sub> reduction are related with oxygen deficiencies which would produce a change in YBCO *c*-lattice parameter (not our case).



Figure 4-10: YBCO critical temperature values in YBCO-BZO nanocomposite films when Y-deficient and Y-compensated precursor solutions have been used.  $T_c$  has been determined from temperature dependence magnetization measurements.

T<sub>c</sub> depression appears to be a general trend for both non-stoichiometric *ex situ* and *in situ* nanocomposites [5,9,148-150] films. Nevertheless, in the latter case, the large lattice mismatch (~9%,) between the heteroepitaxial BZO nanorods and the YBCO matrix cause significant stress in YBCO lattice which probably plays also a role in the reduction of T<sub>c</sub> [89]. Therefore, solution-derived nanocomposites have the advantage that T<sub>c</sub> is unaffected by the presence of nanoparticles because they do not induce any macrostress in the YBCO structure (as indicated by the fact that YBCO *c*-lattice parameter remain constant respect to the bulk value). Therefore, the YBCO lattice appears macroscopically relaxed, in contrast to the *in situ*-deposited YBCO-BZO nanocomposites in which tensile stresses are generally observed in YBCO [151].



Figure 4-11: TEM images of YBCO-BZO (10 mol.%) NC film onto STO substrate; a) Low resolution TEM image viewed along the <100> direction, b),c) HRTEM images showing randomly oriented bulky BZO nanocrystal and d),e) Epitaxial interfacial BZO Nps. Insets: FFT of the same area.

As mentioned previously, the different nature of the growth process of the *ex situ*deposited and the *in situ*-deposited nanocomposites lead to a completely different (nano)structure. In general, *in situ*-deposited YBCO-BZO feature self-aligned heteroepitaxial BZO nanocolumns [5,60,80,86,87,152] whereas in the present *ex situ*-deposited nanocomposites, the BZO nanoparticles are found to be dispersed at random within the YBCO matrix (Figure 4-11(a)). From TEM observations, it is inferred that BZO nanoparticles are mainly round-shaped with sizes ranging 10-30 nm. The coherent domain size has also been estimated using the Scherrer formula yielding sizes of 10 (1) nm along the normal direction of the film surface. Moreover, BZO domain sizes remain invariable for different BZO concentrations (4-20 mol%). It must be mentioned that up to now it has not been possible to estimate the domain size (through XRD) along other directions since only the (002) BZO peak has been measured through symmetric 20-scans. Taking into account that only the (001)-oriented BZO particles (those mainly heterogeneously nucleated at the substrate surface) have been probed through XRD, the resultant estimated domain size will be essentially related with interfacial nanodots, thus having no information about the ones located in the bulk of the film. This fact can be the reason why the particle size range obtained through TEM observations is bigger than the estimated coherent diffracting domain size. However, particle sizes are in agreement when we solely evaluated the interfacial BZO population from TEM images, which ranges from 10 to 15 nm.

Figure 4-11 (d) shows a HRTEM image from a typical interfacial nanodot. The FFT of the interfacial area evidence that the BZO Np are coherent with the matrix and the substrate, i.e.: *c*-axis parallel to both YBCO and STO *c*-axes while the [100] BZO axis lies parallel to the YBCO *a* (or *b*) direction. Therefore, the crystallographic relationship with YBCO can be described as follows: (001)BZO // (001)YBCO and [100]BZO // [100]YBCO.

Although the general trend of BZO is to be round-shaped, some interfacial nanoparticles appear with different morphology. Figure 4-11(e) presents a rectangular-shaped nanocrystal which moreover shows slight tilt respect to the substrate normal. Such tilts were observed in a similar system, in which only interfacial BZO nanoparticles were present [153]. In that case, TEM studies revealed that the tilts were originated during the YBCO growth to minimize the chemical contribution to the interfacial energy [154]. The authors pointed that the tilt mechanism may very likely be related to intercalation of non-stoichiometric extra layers associated with movements of partial dislocations. The tilt angle of the nanocrystals would then depend on the particular arrangement of partial dislocations which in turn would explain the coexistence of tilted and non-tilted nanoparticles.

TEM results revealed that the BZO cube-on-cube epitaxial relationship was only maintained near the substrate interface while the nanoparticles embedded within the bulk of the matrix did not exhibit a clear crystallographic relationship with YBCO. Figure 4-11 (c) displays a non-coherent bulk Np and strongly distorted YBCO matrix around it. The disruptions are mostly related with stacking faults (SF), i.e. the periodicity of the CuO planes (brighter lines) is interrupted, shifted vertically or even bent. The presence of multiple and superposed defects is a general feature of these YBCO-BZO nanocomposites. However, it should be mentioned that the degree of disorder was found to vary depending on the region of the film investigated. As a proof, Figure 4-11(b) shows an incoherent BZO Np embedded within the YBCO matrix which albeit it is disordered (mainly SF and bending), it shows clearly less defects than Figure 4-11(c). Taking into account the

local character of TEM, the eventual deterioration of crystallinity due to TEM processing issues and the microstructural complexity of the present nanocomposites it is very difficult to come to a conclusion about the real influence of the incoherent interfaces on the YBCO matrix.

## 4.2.3. Influence of Nanoparticles Content on YBCO Texture

It is worth mentioning that the indispensable YBCO biaxial texture (single-crystalline state) should be kept in the nanocomposites in order to accomplish the performance requirements. Several defects and inhomogeneities in YBCO can deteriorate its sharp texture, e.g. roughness on the underlying buffer layer, a defective substrate and presence of secondary phases, impurities, etc. Although pure YBCO films prepared at ICMAB show a perfect biaxial alignment (i.e. (001)YBCO//(001)substrate and [100]YBCO//[100]substrate) it is indispensable to evaluate whether the presence of the nanoparticles has a detrimental effect regarding the texture quality.

In this section, it is presented an XRD study in order to evaluate the YBCO texture quality and at the same time it is complemented with surface morphology studies, through Scanning Electron Microscopy (SEM).

As previously discussed, YBCO in both nanocomposites, shows exclusively *c*-axis alignment. However the in-plane (azimuthal) orientation cannot be inferred from the  $\theta/2\theta$  diffraction patterns. In turn, such information can be assessed by the measurement of a given asymmetric reflection (e.g. (*h0l*)); setting the appropriate tilt angle ( $\chi$ ) and varying the azimuth ( $\phi$ ) angle, which is known as  $\phi$ -scan. The peak twist range ( $\Delta\phi$ ), which is quantified by the Full-Width Half-Maximum (FWHM) provides the in-plane orientation distribution of crystallites. Likewise, the out-of-plane misorientation spread ( $\Delta\omega$ ) can be evaluated by measuring a certain symmetric (*00l*) reflection while tilting the sample in  $\omega$  ( $\omega$ -scan or rocking curve). Pole figure measurements were also performed to study both the in-plane and out-of-plane YBCO texture in the nanocomposites.

Figure 4-12 displays the  $\phi$ -scan of the YBCO (104) reflection performed in a YBCO-BZO (10 mol.% BZO) nanocomposite. The tilt angle of the sample was set at  $\chi$ =36,9° as for a perfectly *c*-oriented film this reflection might only appear at such tilting. The solely presence of four peaks, 90° apart by crystal symmetry, denotes a unique in-plane orientation. This is a common feature of all the YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposites tested, except for the particular case of YBCO-BZO with 25 mol% BZO as it will be described next.



Figure 4-12:  $\phi$ -scan of the YBCO (104) reflection performed in a YBCO-BZO/LAO (10 mol.% BZO) sample.

In Figure 4-13 are shown the (104)YBCO pole figures of the most concentrated nanocomposites (i.e. 30 mol% Y<sub>2</sub>O<sub>3</sub> and 25 mol% BZO). It must be mentioned that the pole figures of the rest of concentrations are not shown because they were similar to the YBCO reference. In all cases, pole figures confirmed the absence of *a*(or *b*)-axis domains which should be located at  $\chi$ =53°. The main four poles located at  $\chi$ ~37° demonstrate that the film is fully *c*-axis oriented.

Figure 4-13(a) evidence that the YBCO biaxial texture is still preserved even with 30 mol% of Y<sub>2</sub>O<sub>3</sub> content. By contrast, in the case of 25 mol% BZO (Figure 4-13(b)), the in-plane texture showed the presence of a secondary component, being 45°-rotated respect to the main component. Such minor in-plane component (estimated to be less that 5%) corresponds to an orientation relationship: (001)YBCO//(001)LAO and [110]YBCO//[100]LAO. The according lattice mismatch to the substrate would be 4.5%, considering that  $2\times\sqrt{2}$  ayBCO fits with  $3\times$ aLAO. Following the same lattice fit basis, the mismatch to the main [100]YBCO orientation would be 6%.

So, we can state that the perfect YBCO biaxial texture is maintained in the nanocomposites, at least up to 20 mol% of nanoparticles.



Figure 4-13: Pole figures of (104)/(014) reflections of YBCO.

The in-plane misorientation spread was investigated by estimating the FWHM of the peaks in the  $\phi$ -scan.  $\Delta \phi$  values ranging from 1,2° to 1,3° were obtained for both nanocomposites which moreover are comparable to pure YBCO (Table 4-5). We conclude therefore that the in-plane texture is not deteriorated with the presence of the Nps, besides, being independent either of the Np type or content.

Nanocomposite film	Np content (mol.%)	In-plane mosaic Δφ (°)
	0	1.23 (7)
YBCO-BZO	10	1.3 (1)
	20	1.32 (5)
	0	1.23 (7)
YBCO-Y <sub>2</sub> O <sub>3</sub>	10	1,19 (5)
	30	1,24

Table 4-5: Mean In-plane mosaic ( $\Delta \phi$ ) for YBCO-Np/LAO films with different Np content. Values in parenthesis account for the standard deviation.

By contrast, the out-of-plane misorientation shows a different trend. As a matter of fact, Figure 4-14(a) shows the rocking curve of the YBCO (005) peak for YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub> NCs with the same Np concentration (15 mol.%). The estimated FWHM of YBCO-BZO (15mol.%) doubles the FWHM of the YBCO-Y<sub>2</sub>O<sub>3</sub> (15mol.%), signalling that BZO Nps deteriorate the YBCO out-of-plane texture. Moreover, the extent of out-plane mosaic for YBCO-BZO increases monotonically with the BZO concentration reaching values around 1.1° at 25 mol.% BZO, as shown in Figure 4-14(b). By contrast,  $\Delta\omega$  remains almost unvarying (0.4°-0.5°) for the whole range of Y<sub>2</sub>O<sub>3</sub> concentration (0-30 mol%).

Additionally, surface morphology studies through SEM indicate that YBCO-Y<sub>2</sub>O<sub>3</sub> film surface keeps the uniformity in the whole range of concentrations though some sign of strong porosity was observed at very high Y<sub>2</sub>O<sub>3</sub> concentration (30 mol.%, Figure 4-15).



Figure 4-14: a) Rocking curves of the (005) YBCO diffraction peak for YBCO-BZO and YBCO- $Y_2O_3$  (15 mol.%). b) Influence of the Np concentration in the out-of-plane YBCO misalignment. All the samples compared were grown on LAO.

On the contrary, the surface of YBCO-BZO nanocomposites appear to be inhomogeneous as BZO concentration increases and needle-shaped defects were observed at BZO contents ≥15mol.% (Figure 4-16). The composition of such "needles" was found to be YBCO because no change in contrast was detected when imaging (in SEM) the backscattered electrons.



mol.% Y<sub>2</sub>O<sub>3</sub>

Figure 4-15: SEM images of YBCO-Y<sub>2</sub>O<sub>3</sub> NCs with different Np content. Film surfaces appear to be homogeneous though porosity increases at high  $Y_2O_3$  concentrations.



mol.% BaZrO<sub>3</sub>

Figure 4-16: SEM images of YBCO-BZO NC with different Np content. Film surfaces appear to be inhomogeneous as BZO concentration increases

It must be mentioned that the particles present at the surface of YBCO-BZO cannot be considered as defects induced by the BZO. Proof of it is that such aggregates (identified as CuO by EDX and XRD) are also present in the pure YBCO film. Slight YBCO off-stoichiometry (Cu excess) can lead to the nucleation of stable CuO particles which further diffuse to the film surface. Such superficial precipitates are commonly observed in YBCO films regardless the deposition technique [155-157]. However, CuO aggregates do not affect detrimentally the superconducting properties since they are located at the surface thus enabling the percolation of current.

Holesinger *et al.* [158] observed similar needle-shaped defects in the surface of pure YBCO thick films (1-2.4  $\mu$ m) grown by *ex situ* conversion of physical vapour-deposited BaF<sub>2</sub> precursors. In that case, the needle-shaped structures were believed to be indicative of out-of-plane misalignments of YBCO colonies. However, according to the authors, the growth process involved a transient liquid phase, which is a controversial issue. In our case, such liquid-mediated growth was never detected. In spite of the apparent different growth mechanisms, it is very likely that the superficial defects we observed in high-concentrated YBCO-BZO NCs could be also related to *c*-axis YBCO misoriented domains. In addition, this hypothesis would be in agreement with the previous observation of an increase of the out-of-plane spread ( $\Delta\omega$ ) for YBCO-BZO and not for YBCO-Y<sub>2</sub>O<sub>3</sub>, as shown in Figure 4-14.

Earlier investigations in the group [54], showed that out-of-plane deteriorations in pure YBCO films were related to the presence of secondary phases (Ba-Cu-O). Likewise, Holesinger *et al.* [158] found that YBCO grains on top of a secondary phase layer of Ba<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> showed a significant out-of-plane tilt. So, it seems consistent that in our nanocomposites, YBCO tilted domains and the subsequent worsening of the out-of-plane texture may be originated by the presence of nanoparticles (showing BZO the most significant effect).

Sources of out-of-plane misalignment in pure YBCO films have been reported [159] to be mainly related to the substrate, either a tilted structure or other substrate defect. Taking into account that the YBCO-BZO and YBCO-Y2O3 samples evaluated have been grown both onto LAO substrate, it is thus very likely that the *c*-axis misalignment in YBCO-BZO is related with the presence of BZO nanoparticles either located at the substrate interface or within the bulk of the film. However, the arising question is why the Y<sub>2</sub>O<sub>3</sub> particles do not affect the vertical alignment in a similar way. Taking into account that both epitaxial and randomly oriented Nps coexist in the present nanocomposites, it is presumable that their influence on the YBCO texture quality is diverse. Therefore it turns crucial to quantify the nanoparticles' texture in order to correlate the semi-coherent and incoherent interfaces with the distorted YBCO matrix. In addition, the fact that only the out-of-plane texture is deteriorated when increasing the [BZO] while the in-plane alignment spread remain invariable, point that the defects generated by the interaction between YBCO matrix and BZO Nps, affect mainly the *c*-axis direction. For instance the strong buckling of the YBCO crystallographic planes observed in HRTEM images (Figure 4-11) would be in agreement with our assessments. In fact, a recent HRTEM study [154] performed in YBCO-BZO NCs (displaying only interfacial Nps) showed a strong bending of the (001) YBCO planes. Such bending was justified by the fact that the semi-coherent interface between YBCO and BZO was built up in a way that the similar BaO planes of both structures were continuous across the interface, thus diminishing the interfacial chemical energy.

The results presented in this section from both XRD (texture) and SEM (surface homogeneity), reveal some degradation of the film quality when increasing the content of BZO. However, the fact that such quality was very little affected in YBCO-Y<sub>2</sub>O<sub>3</sub>, indicate that both nanocomposites must have a different microstructure-structure landscape. The different nucleation mechanisms of the nanoparticles as well as the different lattice mismatch to YBCO will very likely force a dissimilar scenario in which the crystallographic orientation of the nanoparticles can be strongly affected and consequently the YBCO microstructure. It turns thus necessary to study more
accurately the texture of the nanoparticles in order to understand its influence on the YBCO matrix. Such study will be the focus of the next chapter.

### 4.3. Conclusions

Chemical Solution Deposition (CSD) has demonstrated to be successful for the growth of *in situ* complex oxide nanocomposites with different nanoparticles content (4-30 mol%). No chemical reaction was observed between YBCO and the secondary phases, with exception of Y doping in the BZO structure which did not have any detrimental effect on YBCO once Y was compensated in the precursor solution.

BZO and Y<sub>2</sub>O<sub>3</sub> nanoparticles spontaneously nucleated either at the substrate interface or within the bulk of the film. They were found to be homogeneously distributed with sizes ranging 10-30 nm. As a general trend, those Nps heterogeneously nucleated at the substrate interface an epitaxial relationship with the substrate and with the YBCO matrix showed ((001)Y<sub>2</sub>O<sub>3</sub>[110]//(001)YBCO[100] and (001)BZO[100]//(001)YBCO[100]). By contrast, those Nps located at the bulk of the film were found indistinctly to be epitaxial or non-epitaxial (i.e. randomly oriented). This fact is the key feature which differentiates ex situ-nanocomposites from the in situdeposited ones. In fact, the different growth nature of both techniques makes possible to obtain dissimilar nanocomposites from the viewpoint of the texture and assembling of nanoparticles. In addition, the nucleation temperature of the Nps with respect to that of YBCO is a crucial parameter in CSD, making possible the tuning of the Nps crystallographic orientation. For instance, it was observed that BZO nucleated prior to YBCO growth while Y2O3 did it simultaneously. As a consequence, bulk BZO Nps did not sustain any specific crystallographic orientation whereas Y2O3 ones were mainly epitaxial with YBCO. This distinguishing feature plays an important role in the subsequent YBCO texture quality.

YBCO biaxial texture was maintained in the nanocomposites, though BZO Nps were found to be more detrimental, affecting in particular the out-of-plane texture of the films. In addition superficial defects which can be related to misoriented YBCO domains appeared in YBCO-BZO NCs with concentration  $\geq$ 15 mol%. Therefore we can conclude that BZO Nps have a stronger influence on the film quality than Y<sub>2</sub>O<sub>3</sub>. We understand that this different behaviour may be related to the particular crystallographic orientation of the Nps within the film and the further interaction with the YBCO matrix. Unlike the YBCO out-of-plane orientation distribution, the in-plane texture was hardly affected in both nanocomposites which would be in accordance with defects generated along the [001] direction of the film.

It is evident that a more accurate study of both the Nps texture and YBCO microstructure is required in order to understand the real influence of the Nps in the YBCO matrix.

# 5. Texture Analysis of Nanoparticles in YBCO Nanocomposite Films

As it was shown in the previous chapter, BaZrO<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> nanocrystals in the nanocomposites are either textured or randomly oriented. Therefore, the analysis and quantification of the orientations is of great importance in order to evaluate their effect on YBCO microstructure and consequently on the final vortex pinning properties.

Quantitative Texture Analysis (QTA) is based on the statistical distribution of orientations of the crystallites in a polycrystalline sample. Mathematically, such distribution is represented by the Orientation Distribution Function (ODF) which provides the volume fraction of crystallites that sustain a specific orientation. Unlike TEM analysis, results from QTA are representative of the whole specimen because they are averaged over the probed sample volume, which is also advantageous for multiphase samples containing low volume fractions of a particular phase or weak textures.

In this chapter we show the results obtained from QTA which was applied to the embedded nanoparticles in the nanocomposites. QTA was carried out through calculation of the Orientation Distribution Function using the MAUD software. In addition, we present a new XRD approach, which taking advantage of a 2D-dectector, quantitatively estimates the volume fraction of epitaxial and randomly oriented nanoparticles with no need of calculating the ODF. In order to confirm the results, we also performed QTA using the MAUD software.

Before getting into the results, it would be useful to briefly introduce some basic aspects of QTA through XRD.

## 5.1. Introduction to Quantitative Texture Analysis (QTA)

The term texture refers to a non-uniform orientation distribution (i.e. preferred orientation) of crystallites within a sample. The highest degree of texture is achieved in single-crystals or epitaxial films. By contrast, polycrystalline samples generally show no preferred orientation (i.e. uniform orientation distribution).

Texture may be described as a distribution of vectors in three-dimensional (3D) orientation space. Therefore, for a quantitative evaluation of textures, a 3D description of the orientation distribution (OD) is required. Mathematically, the OD is represented as continuous functions, i.e. the Orientation Distribution Function, named ODF or f(g). The ODF (Equation 5-1) is defined by the volume fraction of crystallites that have the orientation *g* within a certain infinitesimal orientation element *dg*. This definition allows knowing the volumetric fraction of crystallites along any direction of the sample.

$$\frac{dV(g)}{V} = \frac{1}{8\pi^2} f(g) dg$$
 Equation 5-1

In Equation 5-1, the orientation *g* is generally expressed by the three Euler angles ( $\alpha$ , $\beta$ , $\gamma$ ). The Euler angles (Figure 5-1) refer to three successive rotations which transform the sample coordinate system K<sub>A</sub>=(x,y,z) (with the xy plane parallel to the sample surface) onto the crystal coordinate system K<sub>B</sub>=(X,Y,Z). In other words, the Euler angles specify the orientation of a given crystal relative to the orthogonal sample system. Consequently, if the three Eulerian angles are equal to 0, the crystal coordinates would be parallel to the corresponding sample coordinates (e.g. epitaxial film with orientation (001)[100] or cube-on-cube).

As shown in Figure 5-1, to reach a given orientation of the crystal coordinates *XYZ*, the sample coordinate system *xyz* is first rotated about the axis *z* through the angle  $\alpha$  to give x'y'z'.

Then x'y'z' is rotated about y' through the angle  $\beta$  to give x''y''z'' which is also rotated about z'' through the angle  $\gamma$  to give the final *XYZ* coordinate system.



Figure 5-1: Diagram showing how rotations through the Euler angles define the position of the crystallite coordinate system KB=(X,Y,Z) of an orthogonal crystal cell in the sample coordinate system KA=(x,y,z).

When the orientations are represented by the Euler angles, the infinitesimal volume element in Equation 5-1 is:

 $dg = \sin \beta \ d\beta \ d\alpha \ d\gamma$ 

The ODF is measured in m.r.d. (multiples of random distribution) and it is normalized to a value 1 in the case of a perfect uniform distribution of orientations (i.e. random texture):

 $f_{random}(g) = 1$ 

ODF can take values from 0 (absence of crystallites oriented in dg around g) to infinity (for a single crystal or perfect epitaxial texture) in such a way that the integral over all *g* values is normalized to 100% volume. Consequently, the normalization condition of the ODF is that the volumetric sum of all the crystallites over the whole orientation space ( $\Omega$ ) must be equal to  $8\pi^2$ , as described in the next equation:

$$\int_{\Omega} f(g) dg = \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{2\pi} f(\alpha, \beta, \gamma) d\gamma \sin \beta d\beta d\alpha = 8\pi^2$$
 Equation 5-4

Equation 5-2

**Equation 5-3** 

It can happen in a sample, that only a fraction of the total volume is randomly oriented (V<sub>r</sub>) while the rest is textured (V<sub>c</sub>(g)). Then it can be defined  $f_c(g)$  as the texture component or components of the textured volume. The random fraction will produce a uniform "background" level in the ODF, and thus one can decompose the ODF in [112]:

$$f(g) = f_r + f_c(g)$$
 Equation 5-5

, where  $0 \leq f_r \leq 1$ .

By integrating Equation 5-1 and taking into account Equation 5-5, it is obtained:

$$\frac{V_r + V_c(g)}{V} = \frac{1}{8\pi^2} \iiint [f_r + f_c(g)] dg$$
 Equation 5-6

Equation 5-6 verifies that:

 $\frac{V_{\rm r}}{V} = \frac{f_r}{8\pi^2}$ 

$$\frac{\mathrm{V_{c}}\left(g\right)}{\mathrm{V}} = \frac{f_{c}\left(g\right) \, dg}{8\pi^{2}}$$

Consequently, the volume fraction of the randomly oriented crystallites (Vr/V) can be directly extracted from the value of the ODF background normalized to all the orientation space ( $f_r/8\pi^2$ ). In this chapter, we make use of this relationship (Equation 5-7) to determine the randomly oriented fraction of nanoparticles present in the nanocomposites.

Experimentally, ODF cannot be directly measured but it is obtained by the measurement of pole figures (see Chapter 2, section 2.2.2.8 for a description of pole figures). XRD-texture goniometers are only capable of determining the distribution of crystal poles by tilting and rotating the sample in such a way that all possible crystallographic planes are successively brought into reflection condition. However, the projection of a 3D orientation distribution (i.e. ODF) onto a 2D projection plane (i.e. pole figure) results in a loss of information, so that in turn the texture cannot be derived from a given pole figure without some uncertainty. Only when the texture of a sample is strong and well-defined (e.g. epitaxial thin films) may the texture be determined just by inspection of experimental pole figures. By contrast when the texture is poorly defined or contains many components, the ODF needs to be calculated. If a sufficient number of patterns at different

**Equation 5-7** 

rotating and tilting angles are collected, it permits to reconstruct by fitting the entire threedimensional ODF.

The fundamental equation of the ODF computation is the following:

$$P_h(y) = \frac{1}{2\pi} \int f(g) d\gamma$$
 Equation 5-8

, where  $P_h$  is the pole figure of a crystallographic plane h in a certain direction y (identified by the two angles  $\chi$  and  $\phi$ ). A pole figure describes the volume fraction of crystallites having their plane normal (pole) parallel to the sample direction y.

Analogously to ODF, the pole figure of a random sample have the same distribution density, i.e.  $P_h(y)=1$  m.r.d. Integrating  $P_h$  over all the space of the possible orientations we obtain:

$$\int_{y} P_{h}(y) dy = \int_{0}^{\pi^{2}\pi} \int_{0}^{2\pi} P_{h}(\chi, \phi) d\phi \sin \chi d\chi = 4\pi$$
 Equation 5-9

The value obtained in Equation 5-9 permits normalizing the pole figure which is important for quantitative texture analyses.

The calculation of the ODF from experimental pole figures (i.e. solving Equation 5-8) can be achieved through different algorithms which are compatible with the Rietveld Analysis. The first method developed was the so-called Harmonic Method [160] which assumed that both the measured pole figures and the ensuing ODF could be fitted by a series expansion with suitable mathematical functions like *spherical harmonic functions*. However, mathematical limitations of this method might create ghosts (negative and/or unphysical distribution densities) in the ODF. Nowadays the most established methods to compute the ODF (and the ones used in this Thesis) are the so-called Extended WiMV Method [161-164] and the Standard Functions Model [165,166].

EWIMV Method consists of dividing the ODF in a finite number of regular cells (i.e. the regular grid in which the pole figures were measured, typically 5°×5° grid). The ODF is then described by a discrete value of the function inside every cell, being this value refinable through an iterative approach. The main advantage of the EWIMV Method is that operates without needing any parameter to be introduced in the fitting, i.e. no assumptions related with the texture have to be made. The iterative procedure commonly used in EWIMV is schematized in Figure 5-2.



Figure 5-2: Flow chart of the iterative procedure used in EWIMV Method.

By contrast in the Standard Functions Model, the number and location of the texture components need to be manually introduced at the beginning of the refinement, thus requiring a previous knowledge of the texture. Standard Functions Model describes two types of texture: single-crystal and fiber texture. Single-crystal-like texture is defined by the use of spherical components (linear combination of Gauss and Lorentz standard functions) and they are based on the three Euler angles (refinable). In turn, fiber components are obtained by integrating a Gauss spherical component around the fiber axis. This method is specially indicated for very sharp textures with data not covering the entire ODF space.

The main requirement to correctly compute the ODF is the measurement of useful pole figures. Sometimes one single pole figure does not describe the entire orientation distribution and several pole figures would be required for the ODF computation. Moreover, taking into account that the diffracted intensity is proportional to the volume fraction of the considered phase, it becomes complicated to obtain good signal-to-background ratio when measuring pole figures of minor phases or orientations. In general, the lower limit for texture analysis by XRD is ~5 vol.% [167]. For even lower volume fractions, synchrotron sources are then required. Moreover, because of the defocusing effect, sample geometry and absorption, XRD only permits the measurement of incomplete pole figures on flat samples. Complete pole figures can be calculated from ODF even if only incomplete pole figures are measured.

The concentration of nanoparticles in the nanocomposites studied here ranges from 2vol.% to 12vol.%. So, the limitation related with the small volume fraction makes evident that texture quantification of the nanoparticles is not straightforward.

In this chapter we present a new XRD approach in order to quantitatively estimate the fraction of epitaxial and randomly oriented nanoparticles by using a 2D-detector. With this methodology it has been possible to obtain enough signal-to-background ratio with only 1h of measurement and with no need of measuring complete pole figures nor data refinement. In order to confirm the results, we have also performed a quantitative texture analysis based on the calculation of the orientation distribution function (ODF) by using the MAUD software.

Finally, in order to asses all the possible orientations of the nanoparticles, we have measured the full diffraction diagrams for multiple orientations of the sample in order to properly compute the ODF. This methodology requires high number of data (864 diagrams for only one omega position) and thus it is very time consuming. This limitation is even worse in the case of small volume fractions (as is the present case), because it requires also high acquisition times to improve the statistics. However, it represents the most accurate way to evaluate the texture of the nanoparticles.

## 5.2. Quantification of Random/Epitaxial Nanoparticles

As it was shown in the previous chapter, 2D X-ray diffraction patterns are useful to visualize both epitaxial (diffraction pole) and randomly oriented (diffraction ring) phases simultaneously in a standard  $\theta/2\theta$  scan. The diffracted X-rays from oriented crystallites (single-crystal) point to discrete directions each corresponding to a family of diffraction planes (Figure 5-3a)) [168]. On the other hand, the diffraction pattern from a polycrystalline sample forms a series of diffraction cones if a large number of crystals oriented randomly in the space are covered by the incident X-ray beam. Each diffraction cone corresponds to the same family of crystallographic planes in all participating grains. The interplanar distance determines the apex angle of the diffraction cone.



Figure 5-3: Patterns of diffracted X-Rays, a) from a single crystal and b) from a polycrystalline sample [168].

Therefore, an ideal detector should have a spherical detecting surface in order to cover all the diffraction directions in the 3D space, i.e.  $4\pi$  in solid angle as shown in Figure 5-4.



Figure 5-4: Ideal 3D-detector covering  $4\pi$  solid angle [109].

For a flat 2D detector, the detection surface can be considered as a plane which intersects the diffraction cones or poles (Figure 5-5). The sample-to-detector distance determines the resolution and the angular coverage, e.g. higher resolution at high distance or higher angular coverage at short distance. In this work, the sample-to-detector distance has been maintained constant at a value of 15 cm.



Figure 5-5: 2D-detector plane intersecting the diffraction cones/poles.

Quantitative phase analysis through  $\theta/2\theta$  scans in samples containing both single-crystal and poly-crystal is not straightforward. The main limitations are the different diffracting counting time (Bragg condition will be satisfied solely at certain sample orientation for the single-crystalline phases whereas the random ones will diffract at any sample orientation) and the unknown effective diffracting volume. These limitations are however cancelled when dealing only with polycrystalline phases. Consequently, phase quantification of powder samples have become a routine characterization tool by using the Rietveld Method or simply via the integrated intensity ratio (traditional methods) [169].

#### 5.2.1. Quantitative Phase Analysis: Traditional Approach

In this thesis we have developed a methodology in order to quantify the random/epitaxial fraction of a nanoparticulated phase (e.g. BaZrO<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> in epitaxial YBCO matrix grown by an *ex situ* method) which moreover does not need any data refinement. Rather than performing a quantitative **texture** analysis, we propose a quantitative **phase** analysis considering the two orientations (single-crystal and random) of the same phase as two distinct phases.

The strategy is based on the simultaneous out-of-plane measurement of both the diffracted pole (from the epitaxial fraction) and the diffracted ring (from the randomly oriented fraction). Figure 5-6 shows the asymmetric 2D-XRD patterns obtained for both nanocomposites. The incident angle  $\omega$  was fixed to the value of the corresponding maximum intense line of the nano- phase and the detector was centered at the  $\chi$  value of the same line. The  $\phi$  angle was fixed and optimized in order to assure the maximum intensity. In this way, we better visualize the diffracted intensities from both random and epitaxial fractions. That is,  $\omega$ =15°,  $\chi$ =45° and  $\phi$ =0° for the (101) reflection of BZO and  $\omega$ =14.55°,  $\chi$ =55° and  $\phi$ =0° for the (222) reflection of Y<sub>2</sub>O<sub>3</sub>. In this way both epitaxial and random fractions diffract the same counting time which is an essential requirement to get an accurate quantification.

Due to the low volume fraction of the nanoparticles it was necessary to measure during 1h at the fixed  $\omega$  value. Although  $\omega$  was optimized to fulfil the Bragg condition for the (101)-BZO and (222)-Y<sub>2</sub>O<sub>3</sub> planes, the tails of nearby YBCO poles are also detected due to the bi-dimensionality of the detector.



Figure 5-6: 2D-XRD patterns of the nanocomposites measured at fixed  $\omega$  and centered at the maximum intense line of a) Y<sub>2</sub>O<sub>3</sub> and b) BZO.

The epitaxial and random volume fractions were estimated by using the basic equation for the integrated intensity of a reflection *hkl* for a random powder [169] (Equation 5-10).

$$I = I_0 K \lambda^3 V^{-2} m_{hkl} P L v F_{hkl}^2$$

#### **Equation 5-10**

**Equation 5-11** 

, where *K* is a constant that depends on the instrument characteristics, *V* is the volume of the unit cell, *m*<sub>hkl</sub> is the multiplicity of the *hkl* reflection, *P* is the polarization factor, *L* the so-called Lorentz factor, *F*<sub>hkl</sub> is the structure factor and *v* is the effective diffracting volume of the sample, including the effects of absorption. *P* has the form  $(1 + C \cos^2\theta) / (1 + C)$ , where *C* = 1 for an unpolarized beam and *C* =  $\cos^2\theta_m$  if an incident-beam monochromator is used,  $\theta_m$  being the Bragg angle of the monochromator. The Lorentz factor for a random powder, in reflection mode, is of the form L=( $\cos\theta \sin^2 \theta$ )<sup>-1</sup>.

Ideally, the ratio of integrated intensities (once the background has been subtracted) would equal the random/epitaxial volume fraction ratio (Equation 5-11). The rest of the terms in Equation 5-10 are cancelled because we are comparing identical *hkl* reflection of the same phase.

$$\frac{I_{random}}{I_{epitaxial}} = \frac{V_{random}}{V_{epitaxial}}$$

However, the reality is that the measured integrated intensities of both "phases" need to be corrected. On the one hand, the diffracted intensity of the diffraction pole (epitaxial phase) should be normalized for the equivalent 8 poles by symmetry (taking into account the backscattering). On the other hand, the diffracted intensity of the polycrystalline ring should be also corrected for the whole ring (360°) as well as for the entire solid angle  $4\pi$ . The final expression of the integrated intensity ratio is the Equation 5-12, in which  $\Delta \chi = 30^{\circ}$ .

$$\frac{I_{random}}{I_{epitaxial}} = \frac{I_{ring}^{exp} \cdot (360/\Delta \chi) \cdot 4\pi}{8 \cdot I_{pole}^{exp}}$$
Equation 5-12

In the case we are dealing with, however, normalizing the experimental diffracted intensity directly to  $4\pi$  is an approximation because the fraction of solid angle covered by the "random phase" is unknown. In order to minimize this error, we took small ranges along  $2\theta$  in the integration of the "random phase" intensity (Figure 5-7).



Figure 5-7: XRD diffraction pattern showing the integration limits in  $2\theta$  and  $\chi$ .

We performed several quantification analyses changing the 2 $\theta$  integration limits in order to evaluate the error. The dispersion of the resultant volume fraction was around 4%. Finally, we took the same integration limits ( $\Delta 2\theta$ =1.5° and  $\Delta \chi$ =30°) for all the samples.

Figure 5-8 shows the results of the phase quantification. The fraction of nanoparticles randomly oriented is plotted as function of the nanoparticle concentration for both nanocomposites. As expected from the TEM analysis, most of the BZO do not show any specific texture. Around 80-90% of nanoparticles remain randomly oriented in YBCO-BZO nanocomposites containing 10 mol.% of BZO. By contrast, the random fraction of Y<sub>2</sub>O<sub>3</sub> nanoinclusions decreases down to ~20% in nanocomposites with 10 mol% of Y<sub>2</sub>O<sub>3</sub>. As discussed in the previous chapter, the different degree of orientation may be accounted by the different nucleation process of the nanoparticles within the film. BZO nucleate prior to YBCO, thus the Nps are surrounded by an amorphous and

polycrystalline precursor matrix which determines the non-preferred orientation of the embedded BZO Nps. Essentially, only those BZO nanocrystals nucleated heterogeneously at the substrate interface will be epitaxial. Instead, Y<sub>2</sub>O<sub>3</sub> nanocrystals nucleated mainly concomitantly with YBCO, thus inducing the epitaxy of the Y<sub>2</sub>O<sub>3</sub> throughout the film.



Figure 5-8: Percentage of random nanoparticles present in the YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposites as function of their nominal concentration.

Results obtained from this approach would be erroneous if any preferred orientation within the polycrystalline fraction exists because then the diffracted intensity will not be uniformly distributed along the ring. So, we bear in mind that this quantification is just an approximation that can only be applied in very well defined orientations (single-crystal like or perfectly random textures). More complex textures, by contrast, would require of a previous knowledge of the orientation components. I would like to remark however, that even if it is an approximation, it has been very useful for this Thesis to have the opportunity to asses in a fast way the orientation of the Nps as a first attempt to structurally compare both nanocomposites.

#### 5.2.2. Quantitative Texture Analysis: Computational Approach

In order to confirm the previous results we have performed a quantitative texture analysis by computing the ODF with the MAUD software. The starting experimental measurements were the same as in the previous section (Figure 5-6) but in this case we measured also at various tilting angles. Although coverage of the pole figure from a single image is minimal, the information can be sufficient to determine the ODF and then to reconstruct the pole figures [170]. To make the long story short, it will be only explained the procedure followed for one fixed  $\chi$  and  $\phi$ . Figure 5-9 shows the steps performed with MAUD program starting from the experimental 2D GADDS image of YBCO-BZO (10 mol.%) which was taken at  $\omega$ =15°,  $\chi$ =45° and  $\phi$ =0.

Inside MAUD, in order to get single refinable patterns from the 2D image it is required to perform integration along  $\eta$ .  $\eta$  is the angle which defines the position along the diffraction ring and it has not to be confused with  $\chi$  angle. The latter is related to the sample tilt. So, the integration of the diffraction cone along  $\eta$  will give a straight line rather than a curved one (Figure 5-9(c)). Once the 2D image has been transformed to a 1D and 2D-multipattern Figure 5-9(b,c) it is possible then to apply the Rietveld Texture Analysis (RiTA method) [171]. It is necessary to declare the phases YBCO and BZO (with the appropriate space group and structure) and the method to solve the ODF. In the present case, we used the Standard Functions model because with the EWIMV model the refinement was not successful probably due to the limited number of diagrams measured. Figure 5-9(d) shows the resulting calculated 2D-multipattern using the Standard Functions with spherical components for both YBCO and BZO. Although the calculated pattern matches quite perfectly with the experimental one (at least with the naked eye, which is one of the best way to evaluate the refinement), the reliability factor ( $R_{WP}$ ) of the refinement was ~30%. Typically, acceptable  $R_{WP}$  values are around 10-15%. The fact that only few reflections were measured may probably be the origin of the discrepancy. Moreover many parameters need to be adjusted manually, the most critical ones being those related with the texture and the sample reference. If the sample was not mounted correctly aligned during the measurement we can have displacements in the pattern. For instance, a bad levelling in Z position would give displacements in  $2\theta$ . In this kind of samples, where many parameters are correlated, it is easy to reach false minima. Therefore, instead of performing a Rietveld refinement from the very beginning, it is preferably to vary the parameters manually till one gets a computed pattern close to the experimental one.

Figure 5-10 shows the reconstructed BZO pole figures obtained from the computation of the ODF. Uniform distribution of discrete orientations would correspond to a ODF value of 1 m.r.d. (multiple of random distribution). Orientations with densities above 1 m.r.d. have more lattice planes aligned than a sample with uniform distribution. On the other hand, the minimum values of the ODF (i.e. the background) indicate the volume of the material which is randomly oriented as discussed in Section 5.1 (Equation 5-7).

From the reconstructed pole figures we state that BZO exhibits the cube-on-cube orientation {001} <100>, which corresponds to Euler angles  $\alpha$ =0°,  $\beta$ =0° and  $\gamma$ =0°. Slightly misoriented {001} domains are also observed, with 5° of misorientation from the film normal (i.e.

 $\beta$ =5°). This observation is in agreement with TEM results that showed interfacial-epitaxial BZO nanoparticles tilted 5°-6° from the *c*-axis (Chapter 4, Figure 4-11(e)). Similar BZO misorientations have been also observed by members of our group in YBCO films grown on nanostructured templates [153,154] (i.e. BZO nanodots on top of single crystal substrates). The authors stated that interfacial BZO nanodots may undergo such tilts to minimize the chemical contribution to the interfacial energy with the substrate [154].



Figure 5-9: Steps performed with the MAUD program: a) experimental 2D-image collected with GADDS. The detector was centered at  $\omega$ =15°,  $\chi$ =45° and  $\phi$ =0. Integration along  $\eta$  gives b) multipattern and c) 2D representation of the multipattern. d) Experimental and calculated 2D-patterns, the latter obtained after a fitting procedure (Rietveld refinement).



Figure 5-10: Reconstructed BZO pole figures computed from the ODF. BZO shows three singlecrystal orientation components ({001}, {001}-tilted and {110}) and a random component. Nominal BZO content in the sample was 10 mol%.

The reconstructed BZO pole figures also evidence the presence of a minor single crystal orientation corresponding to the Euler angles  $\alpha$ =0°,  $\beta$ =45°,  $\gamma$ =0°, in other words {110} <100>.

From the QTA it was obtained a minimum ODF value of 0.75 m.r.d., which indicates that 75% of the total BZO volume is randomly oriented. Consequently, the remainder 25% is epitaxial. Specifically, 22% maintain the {001} orientation (19% perfectly *c*-oriented and 3% slightly tilted) whereas the rest (3%) hold the {110} orientation.

Analogous QTA was also applied to YBCO-Y<sub>2</sub>O<sub>3</sub> (10 mol.%) nanocomposite film. Figure 5-11 shows the experimental and calculated 2D-multiplot and the reconstructed Y<sub>2</sub>O<sub>3</sub> pole figures. In this case, the minimum orientation density of 0.13 m.r.d. indicates that 13% of the volume of Y<sub>2</sub>O<sub>3</sub> is randomly oriented. The remaining 87% of the Y<sub>2</sub>O<sub>3</sub> volume is epitaxial, with a single orientation component corresponding to {001} <110> (i.e.  $\alpha$ =45°,  $\beta$ =0° and  $\gamma$ =0°).



Figure 5-11: a) Experimental (at the bottom) and calculated (at the top) 2D multipattern of YBCO-Y<sub>2</sub>O<sub>3</sub> (10 mol.%). b) Reconstructed Y<sub>2</sub>O<sub>3</sub> pole figures from the ODF computation

The quantitative results obtained from QPA (Section 5.2.1) and from QTA are quite in agreement, though the QPA approximation slightly overestimates the random fraction (85% *vs.* 75% for BZO and 20% *vs.* 13% for Y<sub>2</sub>O<sub>3</sub>). We attribute this fact to mainly two reasons: i) the surface fraction of the orientation sphere covered by the diffraction ring is unknown. Although we took small 20 integration limits, we are still overestimating when normalizing for the whole sphere, ii) we are assuming that the intensity of the diffraction ring is uniformly distributed as for a perfect random powder. However, if a preferred orientation within the random fraction exists, the quantification will be overestimated when normalizing for the whole ring. In fact, this situation is what happened in the YBCO-BZO nanocomposite. A priori, assuming a perfect random fraction we estimate that 85% of BZO was randomly oriented. However, when measuring other sample orientations and performing QTA we found that other minor preferred orientations (e.g. {110} and {001}-tilted) coexist thus diminishing the real random fraction down to 75%.

Moreover, one has to keep in mind that the measurements were performed by covering all the out-of- plane orientations ( $\chi$ ) but at fixed in-plane twist angle ( $\phi$ ). Consequently, although the information obtained is representative of the out-of-plane texture nothing can be said about the inplane orientation distribution. Therefore, in order to accurately analyze the texture it is required to measure as many as possible sample orientations and then solve the ODF.

#### 5.3. Texture Analysis by Covering all the Orientation Space: BZO case

The detailed study of the BZO orientations was done in collaboration with Prof. Daniel Chateigner (CRISMAT, Caen) during a PhD research stay.

YBCO-BZO (10 mol%) nanocomposite film was measured with a four-circle diffractometer equipped with a curved position sensitive (CPS) detector. Such detector extends over 120° in 20 enabling the simultaneous acquisition of a full 20 diagram at a certain sample orientation (defined by the angles  $\chi$  and  $\varphi$ ). The incident angle  $\omega$  was fixed at 15° and 21° in order to fulfill the Bragg condition for the (110) and (200) planes of BZO. In order to cover at maximum all the orientation space, the sample was scanned by tilting the angle  $\chi$  of the goniometer from 0° to 55° and the azimuthal angle  $\varphi$  from 0° to 355°, both using a 5° step size with acquisition times of 240s. This measurement (at one fixed  $\omega$ ) represents 864 patterns, i.e. 864 sample orientations. Scanning at smaller step sizes than 5° would have been more enlightening. However, one has to bear in mind the huge number of diagrams and thus the extremely long times that would have been required. Just to illustrate the duration of the experiment I would like to note that the measurement of the 864 diagrams lasted 57.6h (2.4 days), multiplied by two as we measured at two different  $\omega$ positions. That is nearly one full workweek to measure just one sample.

Figure 5-12 shows the experimental XRD patterns obtained. To clarify the representation, in Figure 5-12(a) it is shown just the first 72 diagrams acquired. The sum of all the patterns obtained from scanning the different 864 sample orientations is represented in Figure 5-12(b). MAUD software was again used to treat the experimental data. In this case, we could successfully apply the EWIMV method to solve the ODF giving a reliability factor  $R_{wp}$  of 29%. The refined ODF background value was 0.57 m.r.d., which indicates that 57% of the total BZO volume was randomly oriented. Therefore, the remaining 43% should be oriented. The reconstructed pole figures from the ODF computation showed three texture components, as displayed in Figure 5-13.



Figure 5-12: Experimental diagrams measured at  $\omega$ =15° with a four-circle diffractometer equipped with a CPS detector. a) 72 XRD diagrams resulting from scanning  $\phi$ =0°-355° (with  $\Delta\phi$ =5°) at a fixed  $\omega$ = 15° and  $\chi$ =0°. b) 2D-multiplot obtained by summing all the diagrams measured at different rotation ( $\phi$ = 0°-355°) and tilting angles ( $\chi$ =0°-55°). The total number of diagrams was 864.

The main texture component (4 m.r.d.) is the **{001}-orientation**, i.e. the (001) crystallographic plane parallel to the film surface. This out-of-plane orientation is inferred from the (200) pole located at  $\chi$ =0° and the equivalent 4 poles at  $\chi$ =90°. The in-plane distribution of these domains is clearly deduced from the (110) and (111) pole figures. The remarkable presence of 4 poles in the (111) pole figure located at  $\chi$ ~55° and being 90° apart in  $\phi$  makes evident the biaxial nature of this orientation (single-crystal like). The same conclusion is achieved for the (110) pole figure in which it is observed the expected 4 poles at  $\chi$ ~45° and at  $\chi$ ~90° being 90° apart in  $\phi$ . Therefore we denote this BZO orientation as **{001}<100>**.

A second (and minor) component, is the **{110}-orientation** which is inferred from the presence of a central pole in the (110) pole figure. Note that the intensity of the corresponding poles at  $\chi$ ~35° in the (111) pole figure and  $\chi$ ~55° in the (110) pole figure is quite uniformly distributed along the 360° in  $\phi$  rather than being concentrated as poles. This fact evidences that the nanocrystallites have the azimuth angle  $\phi$  as an orientational degree of freedom resulting then in the so-called fiber texture.

Finally, the presence of a central pole in the (111) pole figure also evidence the **{111}-orientation**. However, the corresponding poles can hardly be observed either in the (110) or in the (200) pole figure. Consequently, we assume that the intensity coming from this very minor orientation component is homogeneously in-plane distributed and very likely it will be masked by the background.



Figure 5-13: Reconstructed BZO pole figures from the ODF calculation (EWIMV method).

It is well-known that in thin films, fiber textures with the fiber axis parallel to the sample normal arise when polycrystalline or amorphous substrates are used [172,173]. Taking into account the minor influence of the substrate, the out-of-plane texture is formed mainly by anisotropic growth. Recently, Morales *et al.* [174] observed a fiber texture in ZnSe films due to the presence of an amorphous thin layer of ZnSe on top of the substrate.

In our case, taking into account that randomly oriented BZO nanoparticles were nucleated within the amorphous and polycrystalline precursor matrix, the fiber texture of the {110} and {111} components may be very likely originated from randomly oriented BZO nanocrystals which further reorient. Crystallographic reorientations are commonly observed in oxides (e.g. indium tin oxide (ITO) and CeO<sub>2</sub>) nanocrystals dispersions as a prelude of a coalescence process [175,176]. The driving force of such reorientations is to decrease the interfacial energy being eased when the particle size is small enough (e.g. <~ 5nm) [175].

In the present case, BZO nanocrystals are bigger than 5 nm. Besides, they are also sterically hindered by the surrounding precursor matrix and the rapid advancement of the growth front (typically at a rate of 3-4 Å/s) [177]. However, we believe that a small fraction could still reorient during the YBCO growth. Very likely, the advancement of the growth front pushes the BZO nanocrystals reorienting them along the direction of the film growth (// *c*-axis), thus leading one rotational degree of freedom around that direction (i.e. the fiber axis). A similar situation was observed [178,179] some time ago in melt textured YBCO composites where, BZO, Ag and Y<sub>2</sub>BaCuO<sub>5</sub> (211) inclusions were pushed out the YBCO single domain along the growth front direction. Only those particles with sizes higher than a critical radius (calculated through the

pushing-trapping theory [180]) became trapped in the solid, otherwise they were pushed by the growth front [181,182].

The reason why the [110] and [111] out-of-plane texture components are obtained after reorientation may be explained by a relaxation mechanism in order to diminish the interfacial energy (from incoherent to semi-coherent interfaces). The resultant vertical mismatch between BZO and YBCO domains would be only ~ 1.5% for the  $\{110\}^{BZO}$  orientation and 3.6% for the  $\{111\}^{BZO}$  if one assumes that DME (Domain Matching Epitaxy) model is valid. DME model consider the possibility of an epitaxial relationship between highly mismatched domains when an integer multiple of lattice planes match across the interface [183]. This model has been successfully applied for instance to the epitaxial system (001)[110] (Ce,Gd)O<sub>2</sub> // (001)[100] LAO [75].

In the present case, the vertical matching of the {110} and {111} BZO domains with the {001} YBCO domains may be achieved because 4×d(110)<sup>BZO</sup>~d(001)<sup>YBCO</sup> and 5×d(111)<sup>BZO</sup>~d(001)<sup>YBCO</sup>. By contrast without taking into account DME, the resultant vertical mismatch would not have any physical meaning (>15%). In Figure 5-14 it is sketched the possible interfaces arisen from the vertical matching of the [001] YBCO domains with the [110] and [111] from BZO. We used a solid spheres model and considered only the matching between oxygen sub-lattices because in fact it is the typical model assumed in oxides [184]. In-plane orientation relationships were chosen arbitrarily to be cube-on-cube with YBCO for clarity.

A highly disordered interface is observed for the case of [110]-oriented BZO (Figure 5-14(a)), being the matching achieved at 4 distances of (110) *d*-spacing. Very likely, the disordered interface will reconstruct by generation of defects such as vacancies and dislocations. By contrast, the interface arisen between the [111]-oriented BZO and YBCO occur to be more ordered showing also high alignment of planes through the whole interface. In this case the formation of misfit dislocations would very likely be the mechanism of strain relaxation. HRTEM would be very helpful to locally study such interfaces.

Just to exemplify the importance of vertical interfaces, we would like to mention that vertical (i.e. out-of-plane) mismatch strongly influence the physical properties of the so-called vertical nanocomposite films (e.g. La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>-ZnO [4], BiFeO<sub>3</sub>-Sm<sub>2</sub>O<sub>3</sub>[4], BiFeO<sub>3</sub>-CoFe<sub>2</sub>O<sub>4</sub> [185], BaTiO<sub>3</sub>-CoFe<sub>2</sub>O<sub>4</sub> [2], La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub>-MgO [3,186]). The matching between the self-assembled nanostructures (nanocolumns) dominate the overall strain state of the film, rather than the in-plane mismatch with the substrate, becoming thus a key parameter to control the enhanced functionalities of such nanocomposites.



Figure 5-14: Solid spheres model showing the orientation relationship a) (011)[0-11]<sup>BZO</sup>// (001)[010]<sup>YBCO</sup> and b) (111)[-101]<sup>BZO</sup>// (001)[010]<sup>YBCO</sup>. Vertical matching of the oxygen sub-lattices across the interface (grey line) takes place at every a) 4×d(011)<sup>BZO</sup> and b) 5×d(111)<sup>BZO</sup>. For explicitness, it is also shown the BZO unit cell with the given orientation in each case. In addition, YBCO cell on the right-hand side of the interface only shows atoms located within the plane (100). The ionic radius of spheres is reduced up to 50% for a better visualization.

Although in the present case, it was not possible to quantify the texture components with QTA, the results are very useful to at least qualitatively evaluate the orientations of the BZO nanoparticles both in-plane and out-of-plane. The richness of BZO orientations such as epitaxial, fiber textured and randomly oriented (being the latter the most significant) turn the YBCO-BZO nanocomposites into a promising superconducting material in which highly disordered semi-coherent and incoherent interfaces coexist. A priori, the YBCO lattice distortions induced by the above mentioned interfaces could very likely act as effective vortex pinning centers. Next chapter

will be devoted to the study of the induced YBCO lattice distortions and their correlation with the superconducting properties in both YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposites.

#### 5.4. Conclusions

Quantitative Phase Analysis (QPA) is a fast and straightforward approach to evaluate, and quantify the orientation of nanoparticles in different nanocomposites. However, QPA should only be applied to simple and defined textures which in addition need to be previously known (e.g. from pole figure measurements). Given that preliminary studies about the nanoparticles' texture in the present YBCO nanocomposites (through pole figures and TEM analysis) pointed to a single texture component plus a random fraction, QPA can be successfully applied. Results were dissimilar for both types of nanocomposites. BZO nanocrystals were found to be mostly randomly oriented within the epitaxial YBCO matrix. By contrast  $Y_2O_3$  nanocrystals showed predominantly an epitaxial relationship with the surrounding matrix. These different texture characteristics are explained by the different nucleation temperature of the nanoparticles with respect to YBCO film growth (Chapter 4, section 4.1). Although QPA has been very useful to quantify the random and epitaxial fraction of the nanoparticles, the analysis is still limited regarding a more accurate evaluation of eventual preferred minor orientations as well as the assessment of the in-plane texture. Therefore the best strategy to accurately determine all the possible texture components is performing a Quantitative Texture Analysis (QTA) using a Rietveld refinement procedure (MAUD program). QTA was applied to two different kinds of measurements: i) GADDS measurements in which XRD pattern was obtained by tilting the sample at different  $\chi$  angles but maintaining a fixed in-plane ( $\phi$ ) rotation position and ii) CPS measurements in which the sample was tilted and rotated in a way that all the possible sample orientations were covered.

Comparing the results from GADDS and CPS measurements performed in YBCO-BZO nanocomposites we arrive to very similar conclusions regarding the out-of-plane texture components. Besides the weight of the {111}<sup>BZO</sup>-orientation which very likely is insignificant, the remaining orientations ({001}<sup>BZO</sup>, {110}<sup>BZO</sup> and the randomly oriented one) were identified through both measurements. This fact confirms the suitability of the Quantitative Texture Analysis through the novel GADDS measurements approach. In addition, GADDS measurements have the advantage of using smaller step sizes when integrating along  $\eta$  (i.e. 0,5°) which made possible the identification of {001} domains tilted 5° out-of-plane. By contrast, such domains were not detected with the CPS measurements because the resolution grid ( $\Delta \chi = 5^\circ$ ) was of the order of the texture

distribution, loosing then the information. However the main advantage of the CPS measurements with respect to the GADDS approach is the information obtained about the in-plane texture. Thanks to the calculation of the ODF (EWIMV method) we proved that the secondary BZO texture components {111}<sup>BZO</sup>, {110}<sup>BZO</sup> did not show any preferential in-plane orientation, indicating that "random" nanoparticles could undergo a reorientation.

It would be interesting to extend the above mentioned analysis (study of the Nps texture through the measurement of all the possible sample orientation) to YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposites. Although Y<sub>2</sub>O<sub>3</sub> nanocrystals hold mostly a single epitaxial relationship with YBCO, it is very likely that other minor texture components are present as well as some preferred orientations within the random fraction due to further reorientations as in the case of BZO.

It is noteworthy to mention that any detailed study of the nanoparticles' texture in nanocomposites grown by *ex situ* techniques was reported up to now. Thus, the results here presented are of great importance because they demonstrate the richness of crystallographic orientations of the embedded nanoparticles and that some degree of orientation occurs probably to decrease the high energy of incoherent interfaces. Moreover, the coexistence of semi-coherent and incoherent interfaces very likely affects the YBCO texture differently. Taking into account results from Chapter 4 (section 4.2.3) related to the YBCO texture deterioration due to the presence of Nps and results from the current chapter related to the quantification of the Nps orientation, we can correlate the deterioration of the film texture with the presence randomly oriented Nps (mainly BZO). A part from merely deteriorate the YBCO texture, we believe that the highly disordered semi-coherent interfaces (those arisen from reorientations) as well as the high energetic incoherent interfaces will also play a role in the YBCO microstructure as a result of their mutual interaction.

As a general trend, all the nanocomposites grown by *ex situ* solution-derived techniques will very likely show a similar behaviour than the one described here. That is, the secondary nanoparticulated phase, if randomly oriented, may develop a texturization due to the principal epitaxial phase. This reorientation of nanoparticles in *ex situ* nanocomposite films can be regarded as a previous stage of a fully texturization effect (both-out-of-plane and in-plane). Theoretically, if nanoparticles were smaller enough and if the kinetics were sufficiently high, *ex situ* nanocomposites will very likely resemble to *in situ* nanocomposites regarding the fully texture state of the nanoparticles, which opens a future perspective for the study of new nanocomposites via *ex situ* methodologies. Moreover, it is not nonsense to believe that self-organization processes could undergo in *ex situ* films if the molar fraction of the nanoparticulated phase was high enough (e.g. ~50 mol%) and the nucleation temperature was similar to that of the matrix. In these

conditions, heterogeneous nucleation at the substrate would occur simultaneously and the higher content of secondary phase would favour the further epitaxial growth. Higher concentrations than 30 mol.% have not been tested in the present work (they are detrimental from the properties viewpoint), though examples of other materials are reported in the literature (i.e. La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub>)-MgO) [3,186]. So, it would be interesting to explore such concentration ranges at least from the structural point of view.

# 6. Microstructural Analysis of the YBCO Nanocomposites by XRD: Correlation with Vortex Pinning Properties

Deviations of an ideal atomic structure, generally known as microstructure, can profoundly influence the physical, mechanical and chemical properties of crystalline materials [1,159,187-190]. Therefore, microstructural analysis turns to be indispensable in order to accurately characterize the real structure and further correlate it with materials' properties.

Regarding to the present nanocomposite films, the different crystallographic orientations of the embedded nanoparticles will very likely influence the YBCO microstructure in a different way. The fact that Y<sub>2</sub>O<sub>3</sub> nanocrystals are essentially epitaxial whereas the BZO ones remain mostly randomly oriented evidence that the Np-YBCO interface will differ in terms of coherency and interfacial energy. It is well known [94], that the interfacial energy increases as losing the crystallographic coherency between the involved phases. Taking into account that the minimization of the interfacial energy is strongly related with the generation of lattice defects [84,94] it becomes crucial to characterize the microstructure of the present nanocomposites. Moreover, the lack of knowledge of the induced nano-defects which improve the vortex pinning capabilities in this kind of materials makes even more evident the need of this study.

In this chapter, it will be first introduced some basic concepts of lattice distortions (named strains) and their influence on XRD lines and on superconducting properties. Next, we present a detailed microstructural analysis of the YBCO matrix in both YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub>

nanocomposites. Such study has been carried out by quantifying the distortions of the YBCO lattice through well-established XRD methodologies based on the diffraction-line broadening. We have used isotropic methods ((*hkl*)-independent broadening) like Williamson Hall plot to determine the disorder parameters along the *c*-direction. On the other hand, the (*hkl*)-dependence of the broadening has been investigated by probing different crystallographic directions. In that case we used the MAUD Program to refine the microstructural parameters. The advantage of using MAUD is that both isotropic and anisotropic models for the peak broadening are considered. Although TEM could also provide complementary microstructural information we have mainly focused on XRD analysis. The reason is that the interpretation of TEM investigations in the current nanocomposites is not straightforward due to the severe superposition of crystalline defects together with the presence of nanoparticles. Moreover, in contrast to XRD it is not an easy task to detect interplanar spacing fluctuations representative enough for the whole sample volume. Nevertheless, a limitation of the XRD methods is the impossibility to individually indentify the type of defects that provoke the lattice disorder. On the other hand, XRD is a fast and non-destructive technique, free of possible artifacts due to sample preparation.

Finally, superconducting properties will be also presented in this chapter. Vortex pinning properties of both nanocomposites will be discussed in terms of lattice disorder and Nps' orientation. And last but not the least, the anisotropy of the vortex pinning properties will be described leading to a concluding correlation with the anisotropy of the lattice distortions.

#### 6.1. Introduction to Strain: length scale and its influence on superconducting properties

Analysis of *stress* by means of XRD is based on the measurement of the induced *strains*. Precisely, the strains measured by XRD are mostly induced by residual stresses which are those acting in a solid body free of any external force. Taking into account that the net force and moment on a solid body in equilibrium must be zero, the residual stresses must be balanced within the body. That means that a compressive stress in one part of the body must come with a tensile stress in another part. There are many causes of residual stresses in thin films, typically: i) Mechanical processing ii) Mismatch between film and substrate which leads the so-called *misfit-induced stress*. iii) Difference between the coefficients of thermal expansion of the film and substrate which leads to the so-called *thermal stress*. And finally, iv) crystallographic defects.

Residual stresses are generally categorized as macrostresses or microstresses depending on the length scale they are acting. Macrostresses and the corresponding macrostrains are uniform over large distances (from 1 mm to several mm). On the other hand, microstrains vary either from grain to grain (in a range of microns) or from one part of a grain to another, (in a range of 1-100 nm) [109]. Specifically, three kinds of stresses are known (i.e.  $\sigma^{I}$ ,  $\sigma^{II}$ ,  $\sigma^{II}$ ) and they are illustrated in Figure 6-1.  $\sigma^{I}$ , called macroscopic residual stress or simply macrostress, is the stress corresponding to the averaged strains of all the grains in the material. This first kind of strain can be measured by XRD through the shift of the Bragg peaks. The second kind  $\sigma^{II}$ , named microscopic stress, is the stress present in one or a few grains. The corresponding strains depend on the grain orientation thus differing between adjacent grains.  $\sigma^{II}$  causes also a shift on the Bragg peaks but its measurement through XRD is not straightforward (the X-ray beam should be as small as several grains). Finally the third kind  $\sigma^{III}$ , named r.m.s. (root mean square) microstress, deals with the strain variation inside a grain, at atomic scale.  $\sigma^{III}$  is proportional to local defects in the material. The crystal lattice is distorted in the vicinity of a defect causing slight fluctuation of the *d*-spacings. So, by quantifying the resultant peak broadening (through peak profile modelling) it is possible to determine the distortions taking place at the nanoscale level. At the same time, the information obtained is averaged for the whole sample volume, in contrast to equivalent TEM analysis.



Figure 6-1<sup>3</sup>: Definition of macrostress, microstress and r.m.s. microstress in a polycrystalline material. Stress is plotted along the direction x.

Taking into account the different length scales in which strains are present in a crystalline material, we can redefine the terms as: macrostrain (acting on the macroscopic scale, i.e. ~mm),

<sup>&</sup>lt;sup>3</sup> Figure is courtesy of L.Lutterotti

mesostrain (acting on the mesoscopic scale, i.e.  $\sim \mu$ m) and nanostrain (acting on the nanoscopic scale, i.e.  $\sim$ nm). This "updated" terminology permit us to correlate the influence of the strain's length scale on the superconducting properties in a clearer manner. In High-T<sub>c</sub> superconductivity (HTS), the coherence length ( $\xi$ ) is related to the behaviour of single vortices and to the interaction of the vortex's core with nanoscale defects; thus the characteristic length scale is the nanometer. By contrast, the mesoscopic scale in superconductivity corresponds to characteristics lengths of the order of the penetration depth ( $\lambda$ ), or slightly higher. Therefore it considers both the behaviour of the circulating supercurrents of a single vortex, and bundles of correlated vortices with the related shielding currents interacting with mesoscopic defects. In HTS, this length scale spans from tenths to tens of microns. Taking into account the relevant physical phenomena, the strain's length scale to be considered has to be compared with the fundamental characteristics lengths  $\xi$  and  $\lambda$ . So we can correlate the 3 types of strain, above defined, with its influence on the superconducting properties as follows:

-Macroscopic strain in which the length scale ( $\ell$ ) it is much bigger than  $\xi$  and  $\lambda$  ( $\ell >>> \xi$ ,  $\lambda$ ). This type of strain modifies T<sub>c</sub> homogeneously and it has no direct influence on critical currents.

-Mesoscopic strain (in which  $\ell \gg \xi$ ,  $\ell \sim \lambda$ ) modifies T<sub>c</sub> but not homogenously as in the macroscopic scale. Mesostrains have a small effect on vortex pinning properties (i.e. magnetic pinning [191]) but, instead, it can strongly influence the current percolation.

-Nanoscopic strain (in which  $\ell \sim \xi$ ,  $\ell \ll \lambda$ ) can eventually influence the superconducting order parameter given that the length scale is of the order of the coherence length ( $\xi$ ). Therefore, nonsuperconducting regions (T<sub>c</sub>~0) might be inhomogeneously created due to the decrease of the superconducting order parameter. In contrast to the macroscopic scale, T<sub>c</sub> reductions in such nanoscopic scale will not be easily detected by macroscopic physical measurements (magnetic or transport) given that the non-superconducting regions are localized at the nanoscale and shielded by supercurrents.

Another classification of strains deals with their uniformity or non-uniformity depending if the interplanar distances are homogeneously stressed or not. Uniform strain (macrostrain) causes a shift of the corresponding diffracted line. For instance, if the *d*-spacing becomes smaller due to a compressive uniform strain the diffracted peak will be shifted to higher 20 values. Analogously, a tensile uniform strain will shift the peak to lower 20 values. Uniform strain is commonly observed in early stages of heteroepitaxial films growth. Initially, very thin films strain elastically to have the same *d*-spacing as the substrate leading to perfectly matched (coherent) interfaces. As increasing the film thickness, dislocations form near the interface to relax most of the strain produced by lattice mismatch [84]. The YBCO nanocomposites films described in this thesis are fully relaxed and consequently the diffracted peaks do not suffer any appreciable shift (as discussed in chapter 4).

Non-uniform strain (r.m.s. microstrain or nano-strain), by contrast, experimentally broadens the diffracted peak due to fluctuations of the *d*-spacings. It is assumed that expansions  $(d>d_0)$  and contractions  $(d<d_0)$  occur with equal probability and the strain parameter  $\varepsilon = \Delta d/d_0$  is employed to quantify this distortion. Sources of r.m.s. microstrain are related mainly to crystalline defects, e.g. dislocations, grain and twin boundaries, stacking faults, vacancies, inclusions, chemical heterogeneities etc., but also to mechanical deformation or compositional gradients. Hereafter, r.m.s. microstrain (i.e. nanoscale-induced strain) will be only considered in this work and we will refer to it as microstrain, lattice distortions, disorder, or simply strain.

As stated in the introduction of this Thesis, not only lattice distortions cause broadening of the diffracted lines, but also does small coherent domain sizes (from now on denominated simply as size). Generally both effects occur simultaneously in the material and thus it is required to separate their individual contribution from the total broadening. In this chapter we used mainly two XRD methods to deconvolute both size-strain effects. First, we used the Williamson-Hall Plot which is based on fitting the XRD peaks by analytical functions (e.g. pseudo-Voigt). Then separation of both size and strain effects is carried out by taking advantage of their different order dependency of the broadening. The Rietveld Method (using MAUD program) has been also applied. In MAUD, both isotropic and anisotropic size-strain methods are implemented. As isotropic model it was used a method based on the pattern modelling (Integral Breadth Method) followed by a deconvolution in which the contribution from microstrain is assumed Gaussian while the contribution from finite sizes is assumed Lorentzian. By contrast, the estimation of anisotropic sizes and strains were carried out with the Popa approach, in which size and strain parameters are developed into spherical harmonics from the Gaussian and Lorentzian contribution breadths.

### 6.2. Microstructural Analysis of the Nanocomposites by XRD

#### 6.2.1. Experimental Considerations

Generally, in epitaxial films, some of the diffracted peaks are overlapped with those of the single-crystal substrate due to their similar interatomic distances. For instance in YBCO/LAO and YBCO/STO systems; the (001) reflections from the substrate are overlapped with the (0031) reflections from YBCO due to 1/3cYBCO~asubstrate. For this reason the use of high-resolution XRD (HRXRD) is desirable to resolve the closely spaced peaks (as close as 0.0001°). Another advantage of HRDRX regarding the microstructural analysis is that the instrumental function is almost negligible and constant over large areas of the diffraction space. Thus HRDRX is a very useful tool to derive reliable and meaningful microstructural information from the width and the shape of the diffracted peaks. But all that glitters is not gold; the diffracted intensity is extremely reduced due to the small divergence of the incident beam. So, the measurements are quite time consuming. Moreover, it is desirable to probe as many family planes as possible in order to obtain microstructural information along the different crystallographic directions. This requirement is easily satisfied in polycrystalline materials as each crystallographic plane of any grain contributes to the diffracted signal at random. By contrast, in epitaxial YBCO films, only the (001) crystallographic planes contribute to the  $\theta/2\theta$  patterns (Bragg-Brentano geometry). It is then straightforward to extract microstructural parameters (domain size and microstrain) solely along the *c*-direction in (00l) oriented films but there is lack of information along other (*hkl*) directions. Therefore it is recommended to use a four-circle diffractometer capable of rotating the sample and thus probing different crystallographic directions.

The measurement of (*hkl*)-diffraction lines of YBCO and further Rietveld refinement were carried out in collaboration with Prof. Chateigner and Prof. Grebille at CRISMAT (Caen). A four circle diffractometer (PANalytical's X'Pert MRD,  $\lambda_1$ =1.5406 Å) was used in high resolution mode (Bartels monochromator, 4-crystals Ge-(220)). The instrumental function was found to be negligible and constant in our experimental conditions, thus it was not necessary to deconvolute the instrumental broadening. We also measured routinely the (001) lines of YBCO using a standard powder diffractometer located at ICMAB (Siemens D5000,  $\lambda_1$ =1.5406 Å and  $\lambda_2$ =1.5444 Å). In this case a quartz standard was measured in order to determine the instrumental broadening.

#### 6.2.2. Williamson-Hall Method: lattice distortions along c-direction

Williamson-Hall (W-H) Method [192] separates graphically the size and strain contribution to the total broadening (integral breadth,  $\beta$ ) thanks to their different 2 $\theta$  dependence. Assuming Gaussian profiles, the W-H equation is the following:

$$\beta_{hkl}^2 \cos^2 \theta = \left(\frac{\lambda}{D_v}\right)^2 + 16\varepsilon^2 \sin^2 \theta$$
 Equation 6-1

,where  $D_v$  is the volume-weighted crystallite size normal to the (*hkl*) plane,  $\lambda$  is the wavelength (in Å) , ε is the microstrain ( $\Delta d/d_0$ ) and  $\beta_{hkl}$  is the physical broadening (once the instrumental broadening has been subtracted) of a given (*hkl*) diffraction line located at 2 $\theta$ .  $\beta_{hkl}$  is expressed in radians. The relationship used in the instrumental correction of the measured integral breadth is shown in Equation 6-2.

$$\beta_{hkl}^{2} = \left(\beta_{hkl}^{2}\right)_{measured} - \left(\beta_{hkl}^{2}\right)_{instrumental}$$
 Equation 6-2

The (001)-YBCO lines measured with HRDRX were the following: (002), (003), (004), (005), (006), (007), (008) and (009). The experimental conditions of the measurements were described in Chapter 2, section 2.2.2.12. The integral breadth and the 2θ position of the measured Bragg peaks were determined by a profile fitting procedure (FullProf program) using pseudo-Voigt functions with a global FWHM, a global eta (proportion of Lorentzian), and a linear background. Figure 6-2 shows an example of the obtained refined profile along with the experimental one of the (006)YBCO from YBCO-Y<sub>2</sub>O<sub>3</sub> (10 mol%) nanocomposite.



Figure 6-2: Experimental diffraction profile (in red), calculated (in black) and difference (in blue) obtained from profile fitting using FullProf.

By plotting  $\beta^2 \cos^2\theta$  versus  $\sin^2\theta$  a straight line should be obtained if both size and strain are isotropic (i.e. (*hkl*)-independent). From the linear fit to the data, the crystallite size is extracted from the *y*-intercept and the microstrain from the slope. Figure 6-3 displays the W-H plots of YBCO-BZO (10 mol.%) and YBCO-Y<sub>2</sub>O<sub>3</sub> (10mol.%) nanocomposites. Pure YBCO film has also been measured for comparison. Since we solely probed the (00*l*) reflections, the resultant microstrain and domain size values provide information only along the film normal. In (00*l*)-oriented films, the domain size along the *c*-axis can be regarded as the film thickness. Therefore, the *y*-intercept of the fitted line will give a measure of the film thickness or rather the coherent domain thickness (which is typically smaller than the geometrical thickness).



Figure 6-3: Williamson-Hall plot from the (001) YBCO lines of YBCO-BZO (10 mol%), YBCO-Y<sub>2</sub>O<sub>3</sub> (10 mol%) and pure YBCO film. The XRD patterns have been acquired in high resolution mode.

As shown in Figure 6-3, the obtained *y*-intercept values  $(\lambda/D_v)^2$  are very small (~5·10<sup>-7</sup>-10<sup>-6</sup>), as expected from the large film thickness (~250 nm). The term large is referred obviously within the XRD context, where sizes greater than 1000 nm are considered infinite thus not contributing to the peak broadening. The domain sizes obtained from the *y*-intercept of the fitted lines are within the range of 173-220 nm, quite in agreement with the geometrical thickness of the films. It should be mentioned that such domain sizes do not show any clear correlation with the microstrain values. This observation is in contrast with results from Scardi *et al.* [102] who observed that domain sizes were inversely proportional to the microstrain in epitaxial YBCO thin films. However they used the Warren-Averbach method (based on the Fourier Analysis) which is more quantitatively accurate than the W-H plot because it does not require an analytical function be ascribed to each reflection [169,193].

In any case, what truly influences the peak broadening in our nanocomposites is not the domain size but the microstrain. Figure 6-3 evidences a significant increase of the slope of the fitted lines (related with the microstrain) whereas the *y*-intercepts remain all close to zero. Therefore we are going to focus basically on the microstrain, i.e. lattice disorder.

A pure YBCO film shows 0.09% of microstrain whereas YBCO-Y<sub>2</sub>O<sub>3</sub> and YBCO-BZO nanocomposites (both with 10 mol% Nps) show respectively 0.13% and 0.25%. That is a microstrain increase of 44% for Y<sub>2</sub>O<sub>3</sub> and 177% for BZO. These results evidence that the presence of nanoparticles in the YBCO matrix provoke distortions of the YBCO lattice along the *c*-axis. In particular, the fact that microstrain is higher for YBCO-BZO than for YBCO-Y<sub>2</sub>O<sub>3</sub> is in accordance with the higher disorder observed by TEM (e.g. (001) planes buckling) and the stronger deterioration of the out-of-plane texture in YBCO-BZO (Chapter 4). To exemplify the latter relationship, it is represented, in Figure 6-4 the microstrain values (//c-axis) obtained for both nanocomposites with different Nps content as function of the out-of-plane misalignment ( $\Delta\omega$ ). Although YBCO-Y<sub>2</sub>O<sub>3</sub> NCs do not show a significant change neither in microstrain nor in  $\Delta\omega$ , the experimental values (in blue) fall in the same linear relation as the YBCO-BZO ones (in red), confirming a correlation between the out-of plane texture quality and the [001]-microstrain.



Figure 6-4: Relation between YBCO microstrain along [001] and the out-of-plane texture spread for both nanocomposites and a pure YBCO film (in green).

The influence of the nanoparticles in the YBCO lattice distortions is further confirmed when analyzing the microstrain of a set of nanocomposites with different Nps' content (Figure 6-5(a)). As increasing the Nps' concentration, the microstrain increases linearly, being this dependence stronger in the case of BZO. This distinct behaviour of both types of nanocomposites leads us to believe that the nanoparticle's orientation may well play a role in the generation of such
distortions. In order to evaluate then the influence of the Nps' texture we plot the microstrain as function exclusively of the randomly oriented Nps' concentration (Figure 6-5 (b)). The collapse of the experimental data indicates that the randomly oriented Nps are those controlling the microstrain development in the YBCO lattice.



Figure 6-5: Influence of the nanoparticles content (BZO and Y<sub>2</sub>O<sub>3</sub>) on the YBCO microstrain (determined from W-H plot). a) Influence of the total concentration of nanoparticles and b) influence of the randomly oriented Nps.

It is not clear at present which is the reason why the random Nps are the responsible of increasing the YBCO disorder. However, these results can be understood if one considers that the interface between YBCO and the randomly oriented Nps is incoherent thus leading to a high interfacial energy. Although incoherent interfaces are little studied, it is well known [84] that the relaxation mechanisms in semi-coherent interfaces involves the generation of lattice defects such as dislocations. Another hypothesis would be the energy relaxation via chemical disorder. We understand as chemical disorder any distortion involving exchanges of atomic positions, e.g. antiphase boundary. There is also the fact that Zr<sup>4+</sup> has been substituted by Y<sup>3+</sup> leading to an excess of Zr in the YBCO matrix capable to produce chemical heterogeneities though a priori Zr does not substitute in YBCO structure. Some examples [144,194] are found in the literature reporting compositional changes and chemical heterogeneities to be the source of microstrain in perovskite materials.

On top of this, TEM analyses pointed that the density of stacking faults (SF) in YBCO-BZO NCs was higher than in YBCO-Y<sub>2</sub>O<sub>3</sub> or pure YBCO films. Stacking faults, occur by intercalation of an extra CuO atomic layer which disrupts the regular stacking sequence (i.e. CuO-BaO-CuO<sub>2</sub>-Y-CuO<sub>2</sub>-BaO-CuO) along the [001] direction, as schematized in Figure 6-6. Consequently the YBCO *c*-lattice parameter in the region of the stacking fault increases from 11,7Å to 13,3Å. If double layers appear rather than a single CuO layer, then the Y<sub>2</sub>Ba<sub>4</sub>Cu<sub>8</sub>O<sub>16</sub> (Y248) phase is formed. Such

intercalation terminates in a partial dislocation (with 1/6 <301> displacement vector) separating a single and double chain layer, with consequent bending of the lattice planes in the area of the dislocation [195] (see Figure 6-6). In addition, antiphase boundaries may form at the termination of a Y248 layer as a mechanism to accommodate the stacking mismatch between the Y248 and the Y123 regions [195]. Usually, stacking faults are regarded to produce either diffraction peak broadening, peak asymmetry or peak shifts [67,95,196,197] though in our case, we solely observed broadening of the (001) diffraction peaks. It is very likely that the peak broadening or asymmetry due to SF is masked in our nanocomposites by the broadening due to the associated dislocations and/or strains. It is worth mentioning that the distortion fields propagation is greater for dislocations than for planar defects. Dislocations affect larger spatial areas because the strain decays as 1/r (being r the distance from the defect) whereas the distortion decays faster for planar defects  $(1/r^2)$  [198]. It is important to mention that stacking faults in YBCO are formed typically during the tetragonal-to-orthorhombic transformation in the oxygenation process [182,199,200]. However, XRD and TEM studies (of samples where the oxygenation process was eluded) confirmed that SFs and the associated in-plane partial dislocations in our nanocomposites are not formed during the oxygenation but during the growth process. In addition the fact that SFs are originated mostly at the YBCO-nanoparticle interface, as shown in Figure 6-7, confirms that the nanoparticles strongly influence the YBCO microstructural evolution during the growth process.



Figure 6-6: Scheme of arrangement of the atomic layers in YBCO crystal with intercalation of one extra CuO layer and the associated edge dislocation.

Moreover, one may interpret that the lateral extent of the stacking faults in the present nanocomposites is likely affected by the presence of the embedded nanoinclusions leading to a complex scenario. Besides, additional strain can very likely be produced by partial dislocations surrounding the stacking faults. For these reasons, it would be very informative to obtain planar view TEM images where the mutual interaction between stacking faults, nanoparticles and inplane dislocations should be detected, similarly to melt-textured grown YBCO-YBa<sub>2</sub>CuO<sub>5</sub> composites [199]. The above mentioned situation appears even more complex if one takes into account the presence of incoherent interfaces which are characterized by a high interfacial energy [94]. Incoherent interfaces separate two dissimilar phases and thus a significant chemical energy contributes to the interfacial energy. In fact, it has been reported [154,201] that a possible mechanism to relax the chemical energy contribution in semi-coherent BZO-YBCO interfaces is by making the BaO planes to be continuous across the interface resulting in a slight bending of the planes. However, in the present YBCO-BZO nanocomposites, the majority of the interfaces are incoherent and very likely the relaxation of the interfacial energy is achieved by introducing lattice defects which at present is not straightforward to individually identify them by TEM due to the complexity of the system. Nevertheless the presence of higher density of planar defects in YBCO-BZO nanocomposites point that a possible mechanism of relaxing the interfacial energy is by means of stacking faults. HRTEM analyses (cross section and planar views) are currently under way to clarify this crucial issue. Preliminary results point at a mutual interaction between YBCO lattice and the BZO nanocrystals resulting in severe YBCO distortions.



Figure 6-7: TEM micrograph showing planar defects (arrows) emanating from a BZO particle.

So, it appears that the superposition of several lattice defects is the distinguishing feature of these solution-derived nanocomposites, being thus a hard task to accurately identify them and even more to understand its origin. However, one can estimate the induced local elastic distortions of the lattice (i.e. displacements of the atoms with respect to their reference positions) by quantifying the XRD peak broadening. In addition such distortions may well be dependent on the crystallographic directions of the given crystal structure, which is known as microstrain anisotropy.

Essentially, W-H method is limited to both isotropic sizes and microstrains being thus not possible to estimate the microstructural parameters in the case they were anisotropic. This fact is

clearly observed in Figure 6-8(a) which displays the W-H plot from both symmetric (001) and asymmetric reflections (*hkl*). In pure YBCO, the additional (*hkl*) data do not follow the tendency of the (001) lines indicating a dependence of the broadening on the crystallographic direction due to anisotropic size or strain. Estimating the microstrain along such (*hkl*) directions require of the measurement of several reflection orders which is not experimentally attainable. However, this representation allows us to assess the peak broadening anisotropy. If the W-H plot results in data dispersion rather than a straight line, it denotes that the broadening is anisotropic (i.e. (*hkl*)-dependent). This is the case of pure YBCO and YBCO-Y<sub>2</sub>O<sub>3</sub> films (see Figure 6-8(a,b)) being thus not feasible to extract the microstrain values for other directions than the film normal. By contrast, data from YBCO-BZO fits correctly in a straight line (see Figure 6-8(c)), denoting that the broadening is not dependent on the crystallographic direction, i.e. isotropic size and isotropic distortions. In this case we can estimate the size-strain values from the W-H plot which are identical to those obtained from just the (001) reflections (Figure 6-3).

Taking into account thus the limitation of the isotropic model used (W-H plot) it is evident the need to apply other methodologies if we want to elucidate the anisotropy of the lattice distortions.



Figure 6-8: W-H plots of pure YBCO and nanocomposite films including (001) and (hkl) lines. Green symbols are data derived from the (113), (123) and (303) lines broadening.

# 6.2.3. Anisotropy of the Lattice Distortions: Rietveld refinement

In order to deeper investigate the anisotropy of the diffraction-line broadening in the nanocomposites and in pure YBCO films, we performed Rietveld refinement by using the MAUD program in which both isotropic and anisotropic models of strain-size are implemented. We used the Delft Model [202] ,which is an Integral Breadth-based method, to model the isotropic peak broadening. Then, anisotropic size and strain parameters are modelled with the so-called Popa

rules [113], which are based on convergent series of symmetrised spherical harmonics. Basis of both XRD methodologies are described in the Appendix (Chapter 8).

The measured diffraction lines were: (002), (003), (004), (005), (006), (007), (008), (009), (113), (103)/(013), (123/213), (303)/(033), (109)/(019), (119) and (129)/(219). Table 6-1 shows the tilting angles where the above-mentioned crystallographic planes are in diffraction condition.

(hkl) (00l)(109)/(019)(129)/(219)(103)/(013)(303)/(033)(119)(113)(123)/(213)χ (°) 0 18,4 25,2 36,7 45 54,7 65,9 71,6

Table 6-1: Film tilting angles ( $\chi$ ) at which the measured diffraction lines are in Bragg condition.

MAUD software enables the refinement of the harmonic expansion coefficients leading to the refined size and strain parameters along all the [*hkl*] directions, even if they were not measured experimentally. The maximum number of coefficients available in the refinement depends on the space group. The strategy used during the refinement was starting always from the isotropic case and if the fitting was not successful, then coefficients related with the deviatory part were added to the refinement until the corresponding fitted value became not significant.

In Figure 6-9 is presented some of the (00l) and (*hkl*) diffraction peaks measured by HRDRX of a pure YBCO film. Although the diffraction lines were measured independently, the refinement was carried out simultaneously for all the peaks ((00l) and (*hkl*)). Blue dots correspond to the experimental data and the solid black line is the fitted profile resultant of applying an isotropic model (Figure 6-9(a)) or an anisotropic one (Figure 6-9(b)). It is remarkable that the peak broadening depends on the (*hkl*) line, increasing with the sample tilting  $\chi$ , i.e. broader peaks as moving away from the film normal towards the film plane. Consequently, in that case the best fit was obtained when applying the Popa rules (Figure 6-9(b)).

It is important to remark that the observed  $\chi$ -broadening is not related to defocusing effects [112] but to microstructural features of the specimen. By using a parallel X-ray beam, defocusing effects were greatly reduced as confirmed by the absence of peak broadening when measuring symmetrical and asymmetrical reflections of the single crystal substrate (LAO).



Figure 6-9: Experimental (blue dots) and fitted (black line) XRD profiles for symmetric and asymmetric reflections of a pure YBCO film. a) Applying an isotropic model (Delft Model) and b) applying an anisotropic model (Popa rules).

In Table 6-2 it is summarized the YBCO structural and microstructural parameters obtained from the Rietveld refinement procedure of both nanocomposites and pure YBCO film. In all cases, the refinement had good quality as confirmed by the low values (9-16%) of the reliability factor  $R_{wp}$  (R-weighted pattern). As expected from previous analysis, the *c*-lattice parameter of YBCO is in accordance with the bulk value (i.e. 11,684 Å) and it does not vary significantly in the nanocomposites denoting that YBCO lattice is not vertically affected by any macrostrain. In turn, *a* and *b* lattice parameters are in agreement with the bulk values (*a*=3,820 Å and *b*=3,885 Å) which confirm also that the film is relaxed in-plane.

Refined microstrain values along [001] ( $\chi$ =0°), [103] ( $\chi$ =45°), and [110] ( $\chi$ =90°) are also shown in Table 6-2. Lattice distortions in pure YBCO films are clearly dependent on the crystallographic direction, being doubled (from 0.05% to 0.1%) when approaching the basal plane. This "intrinsic" anisotropy can be understood by the presence of defects affecting the atomic positions in the plane perpendicular to the sample surface which may very likely be related to dislocations, twin boundaries and oxygen vacancies. This is in agreement with previous microstructural TEM studies [51], performed in our group, which indicated that high density of twin boundaries along [110] and [-110] as well as inhomogeneous dislocation distributions were present in pure YBCO films grown on single crystal LAO substrates. However, such anisotropic character of the YBCO lattice distortions is modified in the nanocomposites, becoming even isotropic in the case of YBCO-BZO. Lattice strain along the [001] direction is increased which would be in agreement with the observation of stacking faults and plane bending mainly in YBCO-BZO nanocomposites.

Film	YBCO lattice parameters (Å)			YBCO microstrain (%)			Domain size (nm)	R <sub>wp</sub>
	а	b	с	[001]	[103]	[110]	Isotropic	(70)
YBCO	3,8261 (1)	3,8881 (1)	11,68341 (4)	0,05182 (1)	0,0614 (2)	0,112 (3)	197 (1)	12.3
YBCO- Y2O3(15%)	3.8253 (1)	3.8876 (2)	11.68534 (7)	0,07391 (1)	0,0792 (4)	0.108 (7)	178 (9)	14.4
YBCO- BZO(10%)	3,8257 (2)	3,8896 (2)	11,6929 (1)	0,107 (1)	0,107 (1)	0,107 (1)	116 (1)	15,9
YBCO- BZO(15%)	3,8222 (5)	3,8916 (9)	11,6858 (1)	0,123 (1)	0,123 (1)	0,123 (1)	106 (1)	9,16

Table 6-2: Refined parameters for the YBCO phase in pure YBCO films and in the nanocomposites (YBCO-Y<sub>2</sub>O<sub>3</sub> and YBCO-BZO). Parentheses indicate the standard deviations on the last digits.

In order to facilitate the visualization of both anisotropic and isotropic microstrains, it is represented in Figure 6-10 the in-plane ( $\varepsilon_{xy}$ ) and out-of-plane ( $\varepsilon_z$ ) components of the microstrain. In the mentioned figure, the refined microstrain values are plotted in a polar coordinate system-like, where the polar angle ( $\theta$ ) goes counterclockwise from the substrate surface plane to the given [*hkl*] direction. As expected from the results of Table 6-2, the plotted microstrain values for the case of pure YBCO and YBCO-Y<sub>2</sub>O<sub>3</sub> (15 mol.%) clearly depend on the direction, thus fitting well with the function of an ellipse. By contrast, for YBCO-BZO nanocomposites the angular microstrain values follow a circular behaviour, denoting isotropic distortions.

Although both Y<sub>2</sub>O<sub>3</sub> and BZO Nps introduce disorder in the YBCO matrix, they affect the anisotropy of the distortions differently. This observation can be interpreted considering the different texture of the nanoparticles which leads to semi-coherent and incoherent interfaces. Although at present, the interaction of such interfaces with the YBCO matrix is unclear, the experimental results indicate that incoherent nanoparticles (mostly BZO) are the ones controlling the microstrain, thus inducing higher disorder in YBCO. This observation was already discussed in (Figure 6-5(b)), where the microstrain was determined through the Williamson-Hall method.

The fact that BZO Nps nucleate prior to the YBCO growth may also play a role in the generation of defects. In fact, it was suggested by some authors [203,204] that lattice defects

(mainly dislocations) were induced when misaligned YBCO growth fronts met. It seems consistent that the density of YBCO front growths will be higher in the case that Nps are already nucleated thus generating more coalescence regions. Consequently, higher density of defects will be introduced.



Figure 6-10: 2D-representation of the microstrain magnitude (obtained from Rietveld refinement) for the nanocomposites and pure YBCO film along different directions.  $\varepsilon_z = \varepsilon \sin \theta$  correspond to the distortions along the [001] direction while  $\varepsilon_{xy} = \varepsilon \cos \theta$  corresponds to the in-plane distortions.

Concerning the domain size, in all cases it was found to be independent of the [*hkl*] direction with values ranging from ~200 nm (pure YBCO) to ~100 nm (YBCO-BZO 15mol.%). The reason why domain sizes are isotropic while strain is anisotropic is not straightforward. It seems that YBCO matrix has an "intrinsic" in-plane microstrain (~ $\epsilon$ =0,10%) which is not affected by the presence of nanoparticles till the [BZO] reaches 15 mol.%. So, distortions induced by the nanoparticles dominate only along the vertical direction whereas the in-plane induced distortion may well be masked by the "intrinsic microstrain". However, both in-plane and out-of-plane-induced distortions appear to reduce the domain sizes in all directions. Diminution of "vertical" domain sizes may very likely be related to the loss of coherence due to the presence of planar defects parallel to the film surface, as earlier suggested by Scardi *et al.* [102]. Therefore in a film free from defects, the vertical domain size would correspond to the thickness of the film. In our case, geometrical film thicknesses were determined to be around 250 nm, well above of the vertical domain size of the nanocomposites (e.g. 106 nm in YBCO-BZO(15 mol.%)), denoting that the defects induced by the nanoparticles reduce the coherent domain size.

In order to summarize the above results, it is represented in Figure 6-11(a), the values of the microstrain and the domain size, obtained from the microstructural Rietveld refinement, as

function of the randomly oriented Nps' concentration. This representation evidences again that randomly oriented nanoparticles are the ones controlling the microstrain evolution in the nanocomposites leading to the generation of lattice strain as a relaxation mechanism of the high interfacial energies. Accordingly, the coherent domain size is reduced due to the induced strain.



Figure 6-11: a) Influence of the concentration of randomly oriented nanoparticles on microstrains (in green) and domain sizes (in orange) along the c-axis direction. Size-strain parameters were determined from Rietveld refinement. b) Correlation of the domain size (//c) with the microstrain (//c).

The inversely proportional relationship between microstrain ( $\varepsilon$ ) and domain size (D) is showed in Figure 6-11(b). This experimental correlation follows the trend already observed in other epitaxial films concerning either loss of coherence by the presence of lattice strain [102] or strain relaxation by lateral grain growth [205]. The first example is analogous to the results here presented, i.e. strains at the nanoscale provoke a diminution of coherent domain sizes. By contrast, the latter case is related to systems in which the strain originates from grain boundaries being thus diminished by island coalescence. The strain dependence on the grain size was numerically modeled by Seel *et al.* leading to the exponential relationship:  $\varepsilon \propto D^{-\alpha}$  [206]. However, our experimental data can be fitted either to a linear or exponential function, given the small range of microstrains.

It must be mentioned that the absolute values of the size-strain parameters obtained from the current analysis (Rietveld refinement) slightly differ from those obtained with the Williamson-Hall (W-H) plot. This observation is not surprising considering that W-H plot is regarded as a semi-quantitative method since it is based in some assumptions [95,193] (e.g. i) profiles are assumed fully Lorentzian or fully Gaussian which is unlikely to occur in practice and ii) size broadening is assumed to be independent on the length of the diffraction vector). More accurate values are obtained with the Integral Breadth method implemented in Rietveld ( i.e. Delft model [202]) because size and strain parameters are extracted from the Lorentzian ( $\beta_L$ ) and Gaussian ( $\beta_G$ ) profile components respectively. Besides, Rietveld method takes into account structural and texture effects which are also included in the refinement. Therefore microstructural values obtained from Rietveld refinement are more exact and thus the ones from W-H are only used in this work as a relative evaluation in series of samples. In addition to the above mentioned, one has to be aware that the quality of the data measurement and the methodology used to deconvolute the instrumental function may also influence the results.

So we conclude that as a result of the introduction of nanoparticles in the films, YBCO matrix appears strongly distorted at the nanoscale as confirmed by the increase of the nanoscaleinduced strain (r.ms. microstrain). In addition, pure YBCO films showed an "intrinsic" microstrain anisotropy which can be tuned by the addition of nanoparticles leading to a complete isotropic strain landscape in the case of BZO.

At this point, we would like to make comment about the different thermal expansion coefficients of YBCO matrix and the nanoparticles. It has been recently found in our group [154] that the different thermal expansion coefficients ( $\alpha$ ) in the *c*-axis direction of YBCO and BZO induce long range-like strain along [001] in YBCO-BZO interfacial decorated films [75]. This strain has been attributed to the anisotropy of the  $\alpha$  values in YBCO, being  $\alpha^{e_{YBCO}} \sim 2\alpha^{ab}_{YBCO}$  (e.g.  $\alpha^{ab}_{YBCO}\sim12\times10^{-6}$  K<sup>-1</sup> and  $\alpha^{e_{YBCO}}\sim23\times10^{-6}$  K<sup>-1</sup> at temperatures of 400°-800°C) [207]. However, in the present YBCO-BZO nanocomposites, the observed microstrain cannot be accounted for such thermal expansion misfit for several reasons. First, if present, the thermal misfit ( $\delta$ ) along the *c*-axis direction would be as low as -0.15 % (at T<400°C) or -1.7% (at T>400°C), both calculated using the expression  $\delta(T)=\Delta\alpha\Delta T$ . Second, thermal misfits usually lead to macrostrain (i.e. peak shifts) rather than microstrain (i.e. peak broadening). In addition, the fact that BZO and Y<sub>2</sub>O<sub>3</sub> have similar and isotropic thermal expansion coefficients in the temperature range of interest (~7.8×10<sup>-6</sup> K<sup>-1</sup>) [208], evidences that the higher distortions in YBCO-BZO should arise from other sources rather than thermal strains.

The results showed in this section represent an important advancement in the study of the complex microstructure displayed by these novel nanocomposites. We stress that these microstrain analyses had not ever been reported for such nanocomposites thus opening the door to further control of the microstructure of these materials. In addition, they enable the understanding of the influence of the microstructure on the superconducting properties, as we describe next.

## 6.3. Superconducting Properties

The study of the superconducting properties of the nanocomposites was carried out by members of our group at ICMAB.

First of all, the superconducting transition temperature (T<sub>c</sub>) of the nanocomposites was investigated for different nanoparticle's concentration (up to 20 mol%). Figure 6-12 evidences that the T<sub>c</sub> values were the expected for an optimal oxygenated YBCO indicating that the microstrain do not influence on T<sub>c</sub>. We remind, however, that YCCO-BZO precursor solutions needed to be Y-compensated to achieve maximum T<sub>c</sub> values, otherwise T<sub>c</sub> decreased due to off-stoichiometries. This issue was already discussed in Chapter 4, section 4.2.2.

The fact that  $T_c$  remains constant in the nanocomposites is a result that differs from those reported for YBCO-BZO *in situ*-deposited, which showed a marked decrease of  $T_c$  being more relevant as increasing the content of BZO [5,60,209,210]. Although, the origin of the  $T_c$  drop in those systems is still unknown, it is believed that it is related to the macrostrain induced by the high lattice mismatch between the heteroepitaxial BZO nanorods and the YBCO, in a similar way that  $T_c$  was decreased in strained YBCO films due to the in-plane mismatch with the substrate [89,211,212].



Figure 6-12: Critical temperature  $(T_c)$  of a set of nanocomposite films as a function of the nanoparticle concentration. Error bars account for the experimental error.

Another superconducting property that merit attention is the critical current density (J<sub>c</sub>). As previously mentioned, J<sub>c</sub> is an extrinsic property which depends on the defects at the nanoscale (controlling the vortex pinning, i.e. the in-field J<sub>c</sub>) and defects affecting the percolation of current (controlling the J<sub>c</sub> at self-field, i.e. no applied magnetic field).

Figure 6-13 shows J<sub>c</sub> values at self-field and at 77K as function of the Nps content for both nanocomposites. Dots account for J<sub>c</sub> mean values of a series of samples while error bars account for the statistical distribution. As observed from the plot, J<sub>c</sub> values increase with the Nps content up to a concentration of 10 mol%, where  $J_c^{sf}$  is maximum in both nanocomposites. YBCO-BZO films (red symbols) show maximum mean  $J_c^{sf}$  values around 5.8 MA/cm<sup>2</sup> whereas YBCO-Y<sub>2</sub>O<sub>3</sub> (blue symbols) show 4.6 MA/cm<sup>2</sup>. The J<sub>c</sub> drop is accounted for the current blocking effect due to the presence of the insulating nanoparticles analogously to the current blocking due to film porosity [137]. So, the trade-off is given at a concentration of 10 mol% of nanoparticle. However, the J<sub>c</sub> drop differs in both nanocomposites showing YBCO-BZO a stronger decrease than YBCO-Y<sub>2</sub>O<sub>3</sub>. This result is in agreement with the fact that randomly oriented BZO Nps not only induced higher disorder in the YBCO lattice, but also deteriorated the texture quality of YBCO and the surface homogeneity (as discussed in Chapter 4). Accordingly, we observed that Y<sub>2</sub>O<sub>3</sub> did influence neither the YBCO texture nor the surface homogeneity thus being J<sub>c</sub> less dependent on the Nps concentration.



Figure 6-13: Critical current density at self-field,  $J_c^{sf}$ , measured at 77K for both nanocomposites with different content of nanoparticles. Dots account for the mean value of a series of samples while error bars account for the statistical distribution.

In general, defects at the mesoscale, that is, defects affecting the current percolation (e.g. bad texture, grain boundaries, porosity, inhomogeneities...) reduce  $J_c^{sf}$  whereas defects at the nanoscale (e.g. crystallographic defects, lattice distortions...) increase  $J_c^{in-field}$ . Therefore a trade-off

is needed to optimize both defects contribution to J<sub>c</sub>. In the next section it will be demonstrated that BZO Nps are the most effective from the pinning viewpoint.

## 6.3.1. Vortex Pinning Properties

Figure 6-14 shows the magnetic-field dependence,  $J_c(H//c)$ , at 77 K measured through transport measurements for YBCO-BZO, YBCO-Y<sub>2</sub>O<sub>3</sub> and pure YBCO films. An overall increase in  $J_c(H)$  occurs, indicating that the vortex pinning properties are improved in the nanocomposites. YBCO-BZO films (red symbols) show better properties than YBCO-Y<sub>2</sub>O<sub>3</sub> (blue symbols) which is in accordance with the higher lattice distortions determined by XRD. In particular, the best properties were obtained for YBCO-BZO films with 10 mol% of BZO displaying record values of  $J_c^{sf}$  (77K)=6.5 MA/cm<sup>2</sup>,  $J_c^{in-field}$  (1T, 77K)=2.2 MA/cm<sup>2</sup> and  $H_{irr}$ (77 K) =10.7 T.



Figure 6-14: Log-log plot showing the magnetic-field dependence of the criticalcurrent density at 77 K for nanocomposites with different Nps' concentration, compared with a pure YBCO film (transport measurements, H//c).

The fact that J<sub>c</sub> becomes less dependent on the magnetic field is more clearly observed in Figure 6-15(a), where the normalized field dependence, J<sub>c</sub>(*H*)/ J<sub>c</sub><sup>sf</sup>, at 50K is shown for various YBCO-BZO NCs films. As increasing the BZO content the J<sub>c</sub> becomes less dependent on the magnetic field which indicates that the presence of BZO Nps efficiently generate vortex pinning centers in the YBCO matrix. For instance, whereas in standard YBCO films at 1T and 50 K, J<sub>c</sub><sup>sf</sup> (*H*) decreases by a factor ~11, in the YBCO-BZO NCs films it decreases just a factor ~4 (Figure 6-15(b). Higher BZO concentrations than 10 mol% do not significantly improve the pinning properties as observed in Figure 6-15(b), which may be very likely related to the detrimental defects at the mesoscale as well as to the diminution of the percolative current paths as pointed out previously.



Figure 6-15: Field dependence of the normalized  $J_c(H)/J_c^{sf}$  at 50 K for pure YBCO and YBCO-BZO nanocomposite films with diverse BZO content (SQUID measurements, H//c). b)  $J_c^{sf}/J_c(1T)$  values as function of the BZO concentration.

Pinning forces ( $F_p$ = J<sub>c</sub>(H) × H) dependences on the magnetic field are represented in Figure 6-16(a). As expected, pining forces are enhanced in both nanocomposites being higher for the YBCO-BZO ones. A record value of ~21 GN/m<sup>3</sup> is observed for YBCO-BZO (10 mol%) at 2T, which is an enhancement of ~175% over *in situ*-deposited YBCO-BZO nanocomposites [5,9,87] and ~60% over NbTi at 4.2K [213] (Figure 6-16(b)). The present pinning force value is the highest ever observed in solution-derived YBCO films. Only nanostructured SmBCO films grown by PLD have achieved values in the same range [214]. Very recently, this record pinning force has been surpassed in a YBCO NC film grown by PLD containing 4 wt.% (i.e. 8 mol%) of BaSnO<sub>3</sub> nanorods [10].



Figure 6-16: Pinning force as function of applied magnetic field along the *c* axis a) at 77K for the pure YBCO and NCs films and b)at 65K and 77K for YBCO-BZO (10 mol%).  $F_p$  of NbTi wires at 4.2K and pure YBCO films at 65K are shown for comparison.

In Figure 6-16(b) it is plotted data from the highest values of  $F_P$  reported for NbTi wires at 4.2K [213] as well as data corresponding to our YBCO-BZO (10 mol.%) at 77K and 65K. For

comparison purposes, the figure also includes the  $F_P$  of a pure YBCO<sup>TFA</sup> film at 65K. The YBCO-BZO nanocomposite film reaches values of  $F_P$ ~78 GNm<sup>-3</sup> at 65 K in a wide (~3–6 T) magnetic-field range, that is, an enhancement of ~500% over NbTi at 4.2 K. These results imply an important scientific and technological achievement because by first time and following a chemical route, YBCO present higher pinning properties than the commonly used NbTi wires.

Further insight into the superconducting properties of the nanocomposite films has been achieved through angular  $J_c(H,T)$  measurements. Figure 6-17 shows the field-angular dependence of YBCO-BZO (red symbols), YBCO-Y<sub>2</sub>O<sub>3</sub> (blue symbols) and pure YBCO films (black symbols) at 77K and 5T along with the configuration used in the measurements (i.e. maximum Lorentz force configuration). It can be noticed, that when the magnetic field, *H*, is closely aligned parallel to the basal plane, a sharp increase of J<sub>c</sub> is obtained in the case of pure YBCO, in agreement with the intrinsic anisotropy of the YBCO material [215-217]. This anisotropic contribution is attributed basically to the intrinsic pinning of the Cu–O planes but also to other extrinsic linear or planar defects lying parallel to the *ab*-planes such as stacking faults [218,219]. In addition, when the magnetic field is applied parallel to the *c*-axis direction a weaker peak is also observed in the J<sub>c</sub>( $\theta$ ) curve of the pure YBCO film (Figure 6-17(a), black symbols). This second peak is attributed to anisotropic pinning centers, in this case, aligned to the [001] direction, such as dislocations or twin boundaries [65,66,220].

It is evident from the  $J_c(\theta)$  curves in Figure 6-17, that J<sub>c</sub> becomes less dependent on the field orientation in the nanocomposites, i.e.  $J_c$  tends to be isotropic, thus pointing at the presence of isotropic pinning centers. In particular, the most isotropic J<sub>c</sub> behaviour is observed for YBCO-BZO (10 mol%). One may think that the nanoparticles itself could act as isotropic defects. However, the high performances obtained cannot be accounted only for the pinning from the nanoparticles itself because the matching field, where the density of defects is equal to the density of vortices would be very low (of the order of some Gauss). Therefore extra isotropic pinning centers must be created in the nanocomposites in agreement with the observed YBCO microstrain and the more isotropic character of such microstrain (section 6.2.3). In addition, the fact that the isotropic character of J<sub>c</sub> increases as the nanoparticle's concentration increases denotes that the nanoparticles induce such isotropic pinning centers. But, how can we evaluate the real contribution of the generated isotropic defects to the total J<sub>c</sub>?



Figure 6-17: a) Field-angular dependence of the critical current density in a log-linear scale at 77K and 5T for YBCO nanocomposites and pure YBCO film. b) Representation of the geometry used in the measurements which ensures the maximum Lorentz force configuration.

Colleagues from the group at ICMAB, have recently developed a methodology [221] based on  $J_{c}(H,T)$  measurements that permits to identify separate and quantify the three basic vortex pinning contributions which are associated to anisotropic-strong, isotropic-strong and isotropicweak pinning centers. On one hand, the separation of the isotropic contribution from the anisotropic one is based on the Blatter scaling approach [222] applied to the  $J_c(\theta)$  data for different magnetic fields at a given temperature. The isotropic defect contribution ( $J_{c^{(iso)}}$ ) to  $J_{c}(\theta, H)$  can be extracted from a plot of the effective field  $H_{\text{eff}} = \varepsilon(\theta)H$ , where  $\varepsilon^2(\gamma, \theta) = \cos^2(\theta) + \gamma^{-2}\sin^2(\theta)$ ,  $\theta$  is the angle between the magnetic field and the film normal and  $\gamma$  is the mass anisotropy ratio (defined as  $(m_c/m_{ab})^{1/2}$ ). The anisotropic contribution  $(J_c^{amiso})$  is in turn determined by subtracting the  $J_c^{iso}(\theta)$ from the experimental  $J_{c}(\theta)$  curve. On the other hand, determination of the strength of the pinning centers is achieved thanks to the different temperature dependences of Jc. HTS materials with weak pinning behaviour usually exhibit an exponential decrease with temperature, i.e.  $J_{c^{wk}}(T)=J_{c0^{wk}}(0)exp(-T/T_0)$ , owing to the low effectiveness of point-like defects against thermal activation of vortices [18]. By contrast, strong pinning centers such as correlated defects, exhibit a smoother temperature dependence, following the expression  $J_{\epsilon^{str}}(T)=J_{c0}^{str}(0)exp[-3(T/T^*)^2$  [18,223]. In both expressions,  $J_{c0}$  is related to the  $J_c$  value in the absence of thermal activation while  $T_0$  and  $T^*$  are related to pinning energy barriers.

Figure 6-18 shows the results of the above mentioned anisotropy-strength study of the pinning centers for a YBCO-BZO (10 mol%) nanocomposite. In particular, Figure 6-18(a) displays the estimated isotropic contribution (red line) and the anisotropic one (blue dots) to the experimental  $J_c(\theta)$  curve (black dots) at 7T and 77K. We notice that except for *H* closely parallel to the film surface, the angular dependence of  $J_c$  fully follows the isotropic defects pinning

contribution (red line). The anisotropic contribution for H//c is estimated to be below ~2% at all temperatures and H <2.5 T. This observation strongly suggests that the pinning centers which cause the high pinning forces in YBCO-BZO films could certainly be isotropic defects.



Figure 6-18: Separation of the different pinning contributions to the critical current density for YBCO-BZO (10 mol.%) a) Isotropic (red line) and anisotropic (blue dots) contribution to the experimental  $J_c(\theta)$ ; b) Weak (in purple) and strong (in pink) contribution to  $J_c^{iso}(T)$ . The solid-dotted (black) line is a fit to the sum of the  $J_c^{wk}(T)$  and  $J_c^{str}(T)$  functions.

The effective anisotropy parameter ( $\gamma_{eff}$ ), obtained from the Blatter scaling approach, is plotted in Figure 6-19 as function of the Nps content for both nanocomposites. In both nanocomposites,  $\gamma_{eff}$  decreases when increasing the Nps content. In particular, YBCO-BZO NCs show the most significant decrease, from  $\gamma_{eff}$ ~7 for a pure YBCO film down to  $\gamma_{eff}$ ~1 with 10 mol% BZO. This phenomenon has never been observed so far in high temperature superconductors. By contrast,  $\gamma_{eff}$  values of YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposites are in the range of  $\gamma_{eff}$ ~3-4. In a recent work [224], it was also reported a  $\gamma_{eff}$  value of ~3 for Sm-doped YBCO coated conductors grown by metal–organic chemical vapor deposition. Nevertheless, the physical reason for this effective anisotropy decrease is still unclear, and further investigations are being pursued to clarify the microscopic origin of this observation.

As was mentioned above, the anisotropic contribution when H//c is very weak, therefore the weight of the strong and weak contributions to  $J_{c^{iso}}(H,T)$  can be easily estimated from either transport or inductive  $J_c(T)$  measurements with H//c at different temperatures and magnetic fields. Figure 6-18(b) shows a typical temperature dependence,  $J_c(T)$ , of a YBCO-BZO (10 mol.%) NC film, from transport measurements at H=1T together with the corresponding fits of the weak and strong pinning contributions. From these analyses, the magnetic-field dependence,  $J_c(H)$ , of the strong and weak pinning contributions were determined indicating that the great enhancement of  $J_c(H)$  arises mainly from the isotropic-strong pinning contribution.



Figure 6-19: Effective anisotropic parameter as a function of the Nps concentration.

The above results can be better visualized if the relative weight of the different pinning contributions (i.e.  $J_c^{iso-weak}$ ,  $J_c^{iso-strong}$ ,  $J_c^{aniso}$ ) is represented for the whole H-T region (H//*c*-axis). Figure 6-20 shows the resultant vortex pinning phase diagrams for pure YBCO film (a-c) and YBCO-BZO nanocomposite (d-f). Different colours/lines represent constant values of the particular pinning contribution to the total  $J_c$  value. So we can immediately ascertain, that the isotropic-strong contribution ( $J_c^{iso-strong}$ ) in the YBCO-BZO nanocomposite film (Figure 6-20(e)) dominates the H-T vortex pinning landscape. The fact that such  $J_c^{iso-strong}$  contribution is also relevant (80% in the worst case) at high fields and high temperatures is surprising since those regions are typically controlled by the anisotropic pinning contribution [225] as it can observed for the pure YBCO film in Figure 6-20(c).

So we can conclude that the YBCO lattice distortions in the nanocomposites have a clear effect on the vortex pinning landscape, varying the relative weight of each defect-pinning contribution if compared with a standard film. Moreover, it has been demonstrated, for the first time, that the isotropic-strong defect contribution is the one dominating the full pinning phase diagram.

A priori, this isotropic pinning, i.e. isotropic pinning centers, seems to be in agreement with the isotropic lattice distortions observed in the case of YBCO-BZO nanocomposite films. In order to confirm this correlation we are going to discuss the pinning properties in terms of microstrain.



Figure 6-20: Vortex-pinning phase diagrams for a pure YBCO film (first line) and a YBCO-BZO (10 mol.%) nanocomposite (second line). a,d) Je<sup>iso-weak</sup> contribution over the Je<sup>total</sup> is indicated at different magnetic fields and temperatures. b,c) H-T maps for the Je<sup>iso-strong</sup>/Je<sup>total</sup> and c,f) for the Je<sup>aniso</sup>/Je<sup>total</sup>.

# 6.3.2. Influence of Microstrain on Vortex Pinning Properties

YBCO-BZO NCs are more efficient than YBCO-Y<sub>2</sub>O<sub>3</sub> ones from the vortex pinning viewpoint. Taking into account that BZO Nps are mostly randomly oriented, it makes sense to believe that incoherent nanoparticles are the ones responsible for the enhanced pinning properties. In Section 6.2.2 it was already discussed that incoherent Nps were the ones controlling the microstrain evolution in the nanocomposites. Therefore, with the aim of correlating the improved pining properties and the disordered YBCO matrix we proceed to plot some of the pinning parameters (i.e. pinning force and effective anisotropy of the superconductor) as function of the microstructural parameters (i.e. microstrain).

In Figure 6-21 is plotted the maximum pinning forces as function of the microstrain (//c) for each nanocomposite. As expected, pinning forces increase with the microstrain. Moreover, the fact that the experimental data of both nanocomposites follows the same tendency proofs that the pinning properties are closely related to the lattice distortions. Therefore, microstrain becomes a valuable tool to control the pinning properties in YBCO films.



Figure 6-21: Correlation between maximum pinning forces and microstrain for both nanocomposites.

It is worth mentioning that one has to be very cautious when comparing absolute values of microstrain because of their possible diverse origin. Similar values of microstrain can be accounted for different type of defects, which can be advantageous or not from the vortex pinning point of view. For instance, colleagues from the group noted that the occurrence of YBCO random fraction in pure YBCO films increased the microstrain but then having detrimental consequences for the superconducting properties. In addition, it is not possible to compare with other techniques like PLD because the processing and the growth mode are completely different. In addition, in *in situ*-deposited films, the epitaxial BZO nanostructures lead to macrostrain values in "similar YBCO samples", e.g. samples which underwent the same processing or with comparable epitaxial quality of YBCO. Having this point in mind, we conclude that in solution-derived YBCO-BZO and YBCO-Y<sub>2</sub>O<sub>3</sub> nanocomposite films, microstrain appears to be a key parameter to control the vortex pinning efficiencies.

The influence of microstrain on the effective anisotropy of the superconductor ( $\gamma_{eff}$ ) is represented in Figure 6-22. An increase of microstrain in the nanocomposites involves a significant decrease of the  $\gamma_{eff}$ , denoting again that the lattice distortions generated in the nanocomposites strongly influence the pinning properties. In this case, the effective anisotropy of the superconductor is the parameter that can be tuned by the induced microstrain.

A further correlation can be established if one considers also the anisotropy of microstrains. We remind that microstrain in pure YBCO films depended on the crystallographic direction (with  $\varepsilon_{xy}/\varepsilon_z=2$ ) and became less anisotropic in the nanocomposites, reaching values of  $\varepsilon_{xy}/\varepsilon_z\sim1$  in the case of YBCO-BZO. This reduction of anisotropy appears to be also related with the diminution of the  $\gamma_{eff}$  as it is shown in Figure 6-23, where the  $\gamma_{eff}$  is represented as function of the microstrain anisotropy parameter,  $\varepsilon_{xy}/\varepsilon_{z}$ .



Figure 6-22: Dependence of the effective anisotropy of the superconductor ( $\gamma_{eff}$ ) on the microstrain. Blue symbols correspond to YBCO-Y<sub>2</sub>O<sub>3</sub> and the red ones to YBCO-BZO.



Figure 6-23: Experimental correlation between the effective anisotropy of the superconductor and the anisotropy of the microstrains.

# 6.4. Conclusions

Two main conclusions can be extracted from this chapter. From one hand, the XRDmicrostructural analyses evidenced that nanoparticles induce high density of distortions in the YBCO matrix changing the intrinsic microstrain anisotropy of the YBCO film. From the other hand, such microstructural disorder has demonstrated to efficiently act as isotropic-strong vortex pinning centers, strongly improving the vortex pinning properties of the nanocomposites without damaging T<sub>c</sub>. The pinning forces achieved in the case of YBCO-BZO (10 mol%) are the highest ever observed in solution-derived nanocomposites. In fact, they were the highest reported in any superconductor at the time the results were published, and they have only been equalled or surpassed by a couple of groups using *in situ*-deposition techniques (i.e. Pulsed Laser Deposition) [78]. Moreover, the isotropic character of the pinning centers (i.e. not dependent on the magnetic field orientation) is a distinctive feature of the solution derived nanocomposites with respect to the *in situ*-deposited ones.

The fact that YBCO-BZO NCs show better performances than YBCO-Y<sub>2</sub>O<sub>3</sub> is attributed to the higher YBCO lattice disorder which is induced by the highly-mismatched semi-coherent interfaces and the incoherent ones. The source of such disorder is not clear at the moment. Dislocations, oxygen vacancies and twin boundaries, are very likely defects that produce microstrain along the direction parallel to the substrate surface whereas stacking faults distort the YBCO lattice along the substrate normal direction. In addition, in-plane partial dislocations are formed at the end of such planar defects. On top of all this, elastic distortions of the YBCO lattice can also be produced without being associated to a particular crystallographic defect, but just as an elastic distortion to diminish the interfacial energy. This latter situation has been observed in YBCO-BZO interfacial decorated films in which long range strain effects without being associated at any particular defect were detected through HRTEM images [154].

The high complexity of the present nanocomposite systems makes the association of the observed microstrain to a particular defect to be a hard task. Cross-section TEM analyses pointed at the presence of several overlapped defects, being stacking faults and plane bending the most significant at first glance. However, TEM images of other regions in the same sample evidenced that such defects were not representative enough while others appear. Therefore it is better to visualize the YBCO lattice distortions as a whole. In this sense, microstrain through XRD is the best parameter to evaluate the YBCO microstructure in these nanocomposites, not only because it gives the average value for the whole irradiated volume but also because its anisotropy can be easily studied. In fact, the investigation of the microstrain anisotropy has made possible to establish a correlation with the diminution of the effective anisotropy of the superconductor.

In conclusion, the results presented in this chapter evidence the great potential of the solution-derived YBCO nanocomposites for applications requiring high magnetic fields. Moreover the fact that J<sub>c</sub> becomes independent on the magnetic field orientation (in the case of YBCO-BZO) turns these nanocomposites to very promising superconducting materials for applications

requiring not only high magnetic fields but also a field rotation (e.g. motors, solenoid magnet). In addition microstrain and its anisotropy have been found crucial parameters in the improvement of the vortex pinning properties. The effective anisotropy of the superconductor as well as the efficiency of the pinning centers, were found to be tuneable by the microstrain which was controlled by the incoherent interfaces. All in all, it has been demonstrated that the angular and field-dependent J<sub>c</sub> performance of YBCO films can be modified by the induced microstrain, thus making possible the design of new nanocomposites with specific applications. The physical origin of the close relationship between microstrain and vortex pinning is, however, an open issue which would require further theoretical analysis.

Further improvement of the superconducting performances in solution-derived nanocomposites could be achieved by controlling the size of the embedded nanoparticles. One approach, being currently investigated at ICMAB, is based on the previous synthesis of nanoparticles and its addition to the precursor solution. In this way, control of the Nps size in the nanocomposites would be straightforward.

# 7. General Conclusions

The study of the Chemical Solution Deposition process led to determine the complete decomposition reaction of the trifluoroacetate precursors, which was unknown up to now. Although the release of HF during decomposition was widely accepted, HF was not detected in the present study. It is noteworthy that the absence of HF in the gas exhaust is advantageous for large scale coated conductors production from both a technical and toxicity viewpoints. In addition, new process conditions have been found to eliminate the porosity in the as-decomposed films. The gas exhaust rate is a key factor to control the residual porosity being the latter strongly reduced by lowering the oxidizing power of the gas flow (from pure O<sub>2</sub> to pure N<sub>2</sub>).

In addition, CSD has demonstrated to be a successful technique for the growth of YBCO nanocomposites with different nanoparticles content (4-25 mol%). Dissimilar nanocomposites from the viewpoint of texture and assembling of nanoparticles have been obtained compared with *in situ* deposited techniques. The most distinguishing features of the present *ex situ* solution-based nanocomposites are the non-epitaxiality with the surrounding matrix and the fact that they do not undergo self-assembling processes. The versatility of the *ex situ* process as well as its crystallization nature allow both the heterogonous and homogeneous nucleation of nanoparticles. In addition, depending on their nucleation temperature, nanoparticles may nucleate prior or concomitantly to the film growth front. This fact along with the lattice mismatch with YBCO has been found to play a decisive role in the final crystalline orientation of the embedded nanocrystals.

The quantification of the nanoparticles' texture together with the study of the YBCO lattice disorder (through XRD methodologies) has been crucial to determine their interrelation. Randomly oriented nanoparticles lead to incoherent interfaces which are the ones controlling the microstructural evolution of the nanocomposites. Incoherent interfaces induce high density of lattice distortions in the YBCO matrix changing also the intrinsic microstrain anisotropy of the film. Such microstructural disorder efficiently acts as strong-isotropic vortex pinning centers, outstandingly improving the vortex pinning properties of the nanocomposites. The pinning forces achieved in the case of YBCO-BZO (10 mol%) are the highest ever observed in solution-derived nanocomposites. Moreover, the isotropic character of the pinning centers (i.e. not dependent on the magnetic field orientation) is a distinctive feature with respect to the *in situ*-deposited nanocomposites.

The results presented in this Thesis evidence the great potential of the solution-derived YBCO nanocomposites for applications requiring high magnetic fields. Moreover the fact that J<sub>c</sub> becomes independent on the magnetic field orientation (in the case of YBCO-BZO) turns these nanocomposites to very promising superconducting materials for applications requiring not only high magnetic fields but also a field rotation (e.g. motors, solenoid magnet). In addition, microstrain and its anisotropy have been found crucial parameters in the improvement of the vortex pinning properties. The effective anisotropy of the superconductor as well as the efficiency of the pinning centers, were found to be tuneable by the microstrain which was controlled by the incoherent interfaces. All in all, it has been demonstrated that the angular and field-dependent J<sub>c</sub> performance of YBCO films can be modified by the induced microstrain, thus making possible the design of new nanocomposites with specific applications.

Of course, there are still certain issues that remain unsolved and should be addressed as further work. For instance, the control of the nanoparticles' size or the knowledge of the particular defects acting as vortex pinning centers. In addition, the reason why the effective anisotropy of the superconductor tends to unity in YBCO-BZO is not straightforward. However, we found experimental evidences that the microstrain anisotropy controls the effective anisotropy of the superconductor.

# 8. Appendix: XRD-Line Broadening Models

Microstructural parameters (i.e. domain size and strain) can be extracted by using either the Integral Breadth or the Fourier coefficients of the XRD-profiles as it will be described next.

# 8.1. Integral Breadth Methods

Methodologies based on the integral breath ( $\beta$ ) require an analytical function to be ascribed to the diffraction profile. Examples of profile functions are the Pearson VII [226], the Voigt [227] and the pseudo-Voigt function [228], being the latter the most used and the one employed also in this Thesis. Pseudo-Voigt function is defined as a summation of Lorentzian (L) and Gaussian (G) functions in the ratio  $\eta/(1-\eta)$ , where  $\eta$  is the Lorentzian fraction ( $\eta$ =1 for pure L and  $\eta$ =0 for pure G):

$$\Omega(2\theta) = \eta L(2\theta) + (1 - \eta) G(2\theta)$$

### **Equation 8-1**

Among the integral breadth methodologies, the so-called Williamson-Hall Plot (W-H) is widely used for its effortlessness. W-H plot is based on the direct summation of both size and strain effects described in Equation 1-6 and Equation 1-7 respectively (defined in Chapter 1):

# $\beta = \beta_S + \beta_M$ Equation 8-2

The experimental integral breadth must be corrected for the instrumental broadening by usually subtracting the integral breadth of a standard sample ( $\beta_{instr}$ ) using one of the following equations [95]:

$$\beta_{corr} = \beta - \beta_{instr}$$

$$\beta_{corr}^2 = \beta^2 - \beta_{instr}^2$$
Equation 8-3

The first equation is suitable for Lorentzian profiles and the second for Gaussian. Since the condition that both profiles, of the specimen and standard, will be pure Gaussian or pure Lorentzian is seldom fulfilled, the use of W-H method should be regarded as an approximation. So, W-H plot is a semi-quantitative method which serves as a measurement of the "relative broadening effect".  $\beta$  is in turn obtained through a profile fitting procedure and the separation of size-microstrain contribution to global broadening is performed graphically given their different dependence in  $2\theta$ . This methodology has been extensively used in the present work and thus a detailed description is given in Chapter 6.

A part from W-H plot, there exist other methods all based in the determination of the integral breadth and further extraction of size-strain contributions. In fact, improved algorithm and software for pattern decomposition and the ability of good quality data from high resolution diffractometers have resulted in a revival of the Integral Breadth methods in microstructural analysis. These methodologies are based on pattern modelling followed by a deconvolution in which the contribution form microstrain is assumed Gaussian while the contribution form size is assumed Lorentzian. Such assumptions are founded on some theoretical and experimental facts which evidence that small-domain-size broadening produces long profile tails of the Lorentzian function and that the lattice-strain distribution is more Gauss-like.

Later on, in the subsection of Rietveld Method, it will be presented the basis of the sizestrain evaluation approaches implemented in the Rietveld refinement procedure.

### 8.2. Warren-Averbach Method

Warren and Averbach [229,230] introduced a method for dealing with combined order independent and order-dependent line broadening. The basis of the method is the multiplicative property of the Fourier transforms of convoluted functions, as is used to remove instrumental contributions from experimental line profiles.

The crystal (assumed to have orthorhombic axes) is represented in terms of columns along the  $a_3$  direction, i.e. the normal direction to the (00*l*) planes. The experimentally observable diffraction intensity may be expressed as a Fourier series being the cosine coefficient of the series the product of two terms:

$$A = A^S \cdot A^D$$
 Equation 8-4

The first term  $A^{S}$  depends only on the column length (size coefficient) and the second term,  $A^{D}$  on distortion in domains (distortion coefficient) and it is order-dependent.  $A^{D}$  is defined as follows:

$$A^{D} = \exp(-2\pi L^{2} \left\langle \varepsilon_{L}^{2} \right\rangle / d^{2}$$
 Equation 8-5

, where  $\langle \varepsilon_L^2 \rangle$  is the mean-squared strain averaged over a distance *L* and *d* is the interplanar spacing. Now Equation 8-5 can be approximated as:

$$\ln A(L) = \ln A^{S}(L) - (2\pi L^{2} \langle \varepsilon_{L}^{2} \rangle / d^{2})$$
 Equation 8-6

By plotting lnA(L) vs  $1/d^2$  it is obtained the size and strain coefficients providing that at least two orders of a reflection were measured. Evaluation of the averaged area-weighted domain size and strain distribution functions is also possible with this methodology.

### 8.3. Comparison between Integral Breadth and Warren-Averbach

Results obtained by the Integral Breadth and Warren-Averbach (W-A) methods are usually not comparable. The former gives volume-weighted domain sizes and upper limit of strain while the latter gives area-weighted domain sizes and mean-square strain averaged over some distance perpendicular to the diffracting planes. Moreover distributions of the microstructural parameters can also be obtained with Warren-Averbach. In addition, W-A gives more accurate results than Integral Breadth methods given that no assumption about the analytical form of diffraction-peak shape is required. By contrast Integral Breadth methods require that size and strain broadening are modelled by either Lorentzian or Gaussian functions and in most cases both size and strain cannot be satisfactorily represented with either function.

It can occur that the line broadening do not only vary as function of the reflection order but also with the reflexion index *hkl* (i.e. anisotropic broadening) which complicates its evaluation. In such cases the above mentioned methods are not satisfactory to describe the *hkl*-dependence and then the so-called Popa approach [113] is used to extract the anisotropic features.

# 8.4. Anisotropic Size-Strain Broadening: Popa approach

Once the size-strain contribution to the line broadening has been modelled with one of the methods above mentioned (i.e. Integral Breadths or Fourier coefficients), Popa approach needs to be applied if an eventual (*hkl*)-dependency on the broadening exists.

Popa models are based on the same basis than Integral Breadth Methods in which the Gaussian component represents the strain effect and the Lorentzian component the size. For size broadening, the radius of the apparent crystallite is expanded in spherical harmonics while for strain broadening some quartic forms in *hkl* are used, both fulfilling the necessary requirement to be invariant to the Laue group operations. The models, which are derived from general crystallographic considerations, are different for each Laue group. The mean crystallite size in the crystal direction *h* is denoted by  $\langle R_h \rangle$  and it is developed in convergent series of symmetrised spherical harmonics with functions:

$$P_{2l}^m(x)\cos m\varphi$$
 or  $P_{2l}^m(x)\sin m\varphi$ 

#### **Equation 8-7**

with 
$$x = \cos \chi$$

, where  $\chi$  and  $\varphi$  are the co-latitude and azimuth angle respectively. The *l* and *m* parameters follow some selection rules [231] and  $P_{2l}^m(x)$  are normalized Legendre functions [113]. As an example, the anisotropic size model for the case of orthorhombic YBCO (Pmmm) is the following:

$$\langle R_h \rangle = R_0 + R_1 P_2^0(x) + R_2 P_2^2(x) \cos 2\varphi + \dots$$
 Equation 8-8

Analogously, anisotropic microstrain is also developed into series. For the specific case of Pmmm symmetry:

$$\langle \varepsilon_h^2 \rangle E_h^4 = E_1 h^4 + E_2 k^4 + E_3 l^4 + 2E4 h^2 k^2 + 2E5 k^2 l^2 + 2E_6 h^2 l^2$$
 Equation 8-9

Popa models for anisotropic line broadening are compatible with Rietveld method. The refinable parameters are the E<sub>i</sub> coefficients of the quartic forms (for anisotropic strains, Equation 8-9) and the R<sub>i</sub> coefficients of the spherical harmonics' series (for anisotropic sizes, Equation 8-8).

# 8.5. Rietveld Method

Initially, the Rietveld Method was devoted to the study of the structure of materials using data from neutron diffraction, but afterwards the method was extended to X-ray diffraction and lately it has became one of the most used tools in both the structural and microstructural study of materials.

Rietveld refinement requires two types of models: a structural model based on approximate atomic positions and a non-structural model which describes the shape of the line profiles in terms of analytical or other differentiable function [111]. The position and intensity of the Bragg reflections are determined by the structural model while the profile shape is determined by the instrumental function and the microstructural effects of the sample. In the absence of microstructural effects, the profile breadth smoothly varies with  $2\theta$  and it is usually modelled by the Caglioti relationship:

$$FWHM = \left[U \tan^2 \theta + V \tan \theta + W\right]^{\frac{1}{2}}$$
 Equation 8-10

, being *U*, *V*, *W* refinable parameters. By contrast the integrated intensity of the peak is only a function of the structural parameters. Then the least squares procedure consists of the minimization of:

$$R_{wp} = \left[ \sum_{i} w_{i} (Y_{io} - Y_{ic})^{2} / \sum_{i} w_{i} Y_{io}^{2} \right]^{\frac{1}{2}}$$
 Equation 8-11

, where  $w_i$  refers to statistical weights and  $Y_{io}$  and  $Y_{ic}$  are the experimental and calculated X-ray diffraction intensity respectively at a given  $2\theta$  angle. The weighted profile factor  $R_{up}$ , is the most meaningful to follow the progress of the refinement.

Simultaneous structure-micro(nano)structure refinements are successfully performed in the Rietveld Method. The refinement of microstructural parameters is based on Integral Breadth methodologies (i.e. Delft Model [202]) which assign the Lorentzian component of the profile to the crystallite size effect and the Gauss component to the strain effect. The volume-weighted crystallite size and strain parameters are extracted from the integral breadth values of the deconvoluted sample profile f(x) using the following expressions:

$$\beta_{L} = \frac{\pi}{\langle D_{V} \rangle \cos \theta}$$
Equation 8-12
$$\beta_{G} = 4 \langle \varepsilon \rangle \tan \theta$$

, where  $\beta_L$  and  $\beta_G$  are the Lorentzian and Gaussian components of the integral breadth respectively.

A more exhaustive description of the Rietveld method is out of the scope of this appendix, but it may be of found in the literature [111].

It is noteworthy to mention that besides Integral Breadth Methods for the isotropic linebroadening model, Warren-Averbach is also compatible with Rietveld. In addition, Popa approach which takes into account the *hkl*-dependence of the size-strain parameters was successfully implemented in Rietveld codes like MAUD [110] or FULLPROF [232].

#### 8.6. Comparison between Williamson-Hall and Rietveld Analyses

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Although both Williamson-Hall plot and Rietveld refinement (Delft Model) are based on Integral Breadths ( $\beta$ ) methodologies, the resultant size and strain values may be different. Such divergence lies on the following reasons: first, the deconvolution methodology for f(x) differs in both analyses. W-H plot uses direct subtraction of the instrumental integral breadth to the experimental one while in Rietveld is used an iterative procedure. Secondly, the model used for the separation of size-strain contribution is also differently defined in both methods. In Rietveld analysis, size and strain parameters are extracted from the Lorentzian component of the integral breadth ( $\beta_L$ ) and from the Gaussian contribution ( $\beta_G$ ) respectively. By contrast, Williamson-Hall analysis assumes that the line profile broadening due to size and strain are fully Lorentzian or fully Gaussian, which is unlikely to occur in practice.

# 9. List of publications

- a. Gutierrez, J.; <u>Llordes, A</u>.; Gazquez, J.; Gibert, M.; Roma, N.; Ricart, S.; Pomar, A.; Sandiumenge, F.; Mestres, N.; Puig, T.; Obradors, X. "Strong isotropic flux pinning in solution-derived YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> nanocomposite superconductor films". *Nature Materials* 2007, 6, 367-373.
- **b.** Pomar, A.; <u>Llordes, A</u>.; Gibert, M.; Ricart, S.; Puig, T.; Obradors, X. "Tuning the superconducting properties of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> tapes grown by chemical methods". *Physica C-Superconductivity and Its Applications* **2007**, 460, 1401-1404.
- c. Obradors, X.; Puig, T.; Ricart, S.; Pomar, A.; Sandiumenge, F.; Mestres, N.; <u>Llordes, A.</u>; Gibert, M.; Gutierrez, J.; Gazquez, J.; Roma, N. . "Nanostructured Superconductor Material of type REBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (RE=rare earth or yttrium) with high density of vortex pinning centres and its preparation method". Patent numbers: WO2008071829-A1; ES2302637-B1; KR2009094121-A; EP2104151-A1; CN101606249-A. **2008**.
- d. Puig, T.; Gutierrez, J.; Pomar, A.; <u>Llordes, A</u>.; Gazquez, J.; Ricart, S.; Sandiumenge, F.; Obradors, X. "Vortex pinning in chemical solution nanostructured YBCO films". *Superconductor Science & Technology* 2008, 21.
- e. Pomar, A.; Vlad, V. R.; <u>Llordes, A.</u>; Palau, A.; Gutierrez, J.; Ricart, S.; Puig, T.; Obradors, X.; Usoskin, A. "Enhanced Vortex Pinning in YBCO Coated Conductors With BZO Nanoparticles From Chemical Solution Deposition". *Ieee Transactions on Applied Superconductivity* **2009**, 19, 3258-3261.
- f. <u>Llordes, A.</u>; Zalamova, K.; Ricart, S.; Palau, A.; Pomar, A.; Puig, T.; Hardy, A.; Van Bael, M. K.; Obradors, X. "Evolution of Metal-Trifluoroacetate Precursors in the Thermal Decomposition toward High-Performance YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Superconducting Films". *Chemistry of Materials* 2010, 22, 1686-1694.

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