Possibility of the existence of fully oxygenated superconducting YBaCuO films with a tetragonal structure

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YBaCuO thin films were deposited *in situ* on $LaAlO_3$ single-crystal substrates by sputtering of a stoichiometric $Y_1Ba_2Cu_3O_7$ target. These films were studied combining ion beam analysis (IBA) techniques with X-ray diffraction measurements at room temperature. Depending on the sample cooling conditions (cooling rate, oxygen pressure), the $\sim$5000 Å thick YBaCuO films can exhibit either an orthorhombic twin phase or a quasi-tetragonal structure. The former is obtained by low cooling rates at high oxygen pressure (0.2–1 bar), whereas the latter needs a rapid quenching to room temperature, even at low oxygen pressures. Our IBA oxygen content measurements show that both kind of samples are fully oxygenated ($\sim O_7$) YBaCuO compounds with T_c onset of 91 K. Moreover, $^4He^+$ channeling studies show that the minimum yield $\chi_{\min}$(Ba) for the quasi-tetragonal films increases with the beam energy. This result seems to indicate that the crystal lattice of these quenched films is subject to some kind of internal strains. From these observations and following thermodynamical considerations, we consider that the formation of YBaCuO thin films with fully oxygenated ($\sim O_7$) tetragonal structure takes place indeed during the high temperature *in situ* growth by cathodic sputtering and these features can be preserved by means of a rapid quenching to room temperature.

Keywords: Superconductors, YBaCuO, structure, thin film

Se depositaron películas delgadas superconductoras del tipo YBaCuO sobre monocristales de $LaAlO_3$ por pulverización catódica de un blanco estequiométrico $Y_1Ba_2Cu_3O_7$. La composición y la estructura de estas películas se estudiaron a temperatura ambiente utilizando técnicas de análisis por haces de iones (ion beam analysis) y difracción de rayos X. Dependiendo de las condiciones de enfriamiento (velocidad de enfriamiento, presión de oxígeno), películas de YBaCuO de 5000 Å de espesor pueden presentar una fase ortorrómbica o una estructura pseudo-cuadrática. La primera estructura se puede obtener combinando bajas velocidades de enfriamiento con altas presiones de oxígeno (0.2–1 bar). En cambio, el segundo tipo de estructura requiere un rápido templado hasta temperatura ambiente, aún a bajas presiones de oxígeno. Ambos tipos de muestras tienen una temperatura crítica T_c del orden de 91 K y están completamente oxigenadas (O_7). Además, estudios por canalización de iones muestran que el valor del cociente $\chi_{\min}$(Ba) aumenta en función de la energía del haz de $^4He^+$ en el caso de películas con estructura pseudo-cuadrática. Este resultado parecería indicar que la estructura cristalina de estas películas está sujeta a algún tipo de tensión interna. A partir de estas observaciones y de acuerdo a consideraciones de tipo termodinámico, consideramos que la formación de películas de YBaCuO con una estructura cuadrática y completamente oxigenadas (O_7) tiene lugar efectivamente durante el crecimiento *in situ* por pulverización catódica y que estas características se pueden conservar mediante un rápido enfriamiento hasta temperatura ambiente.

Descriptores: Superconductores, YBaCuO, estructura, películas delgadas

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1. Introduction

The physical and structural properties of the superconducting YBaCuO compound depend not only on the oxygen content, but also on the oxygen ordering in the Cu-O chain-planes [1]. Moreover, for bulk samples kept on thermodynamic equilibrium conditions, two empirical relationships have been established: namely, the well known two-plateaus relationship of the critical temperature T_c as a function of the oxygen content O_x [2], and that between O_x and the c-axis lattice parameter, which shows that the latter grows when the oxygen content decreases [3]. However, in the case of thin films, the physical properties are also affected specifically by some other factors, such as the substrate material and the sample preparation conditions (substrate temperature and oxygen partial pressure), because thin films are not prepared in thermodynamic equilibrium conditions. On the other hand, plenty of crystalline defects may be introduced during the film deposition, influencing once again the film properties.

Hence, it was observed that in the case of YBaCuO thin films, the c-axis lattice parameter depends not only on the oxygen content, as in bulk material, but also on the growth conditions and lattice defects [4]. We have recently determined that the expansion of the c-axis lattice parameter in the case of thin films with high critical temperatures ($T_c > 80$ K) is not attributable to an oxygen deficiency [5, 6]. Indeed, our oxygen content measurements by RBS (Rutherford backscattering spectrometry) and NRA (nuclear reaction analysis) showed that these films, deposited by inverted cylindrical magnetron sputtering, were fully oxygenated ($O_{6.8}$–$O_{7.0}$), independently of the anomalous c-axis lattice parameter expansion and the oxygen pressure during cooling [6]. Therefore, while the sputtered films are not prepared under thermodynamic equilibrium conditions, it seems rather that they grow with an oxygen content higher than that expected by merely thermodynamical considerations [7], because of the presence of atomic oxygen during the film deposition by magnetron sputtering [6].

YBaCuO compounds are superconducting in the orthorhombic phase and insulating in the tetragonal one. In the case of the ordered orthorhombic structure, the Cu-O chains along the b-axis direction are electron reservoirs for the charge transfer from the CuO_2 planes. Hence, these chains act as dopants for the CuO_2 planes and this fact is essential for the occurrence of the superconductivity. On the other hand, when the distribution of oxygen atoms in the plane of the chains is completely random, the overall crystal symmetry is tetragonal. The tetragonal structure is usually associated to the disorder of oxygen atoms in the Cu-O chain-planes and to the equal occupation of oxygen sites along both a and b axes. In this case, the ordered orthorhombic structure consisting of Cu-O chains along the b-axis disappears and the compound turns into insulator.

It is generally accepted that the YBaCuO compound grows as an oxygen deficient phase with a tetragonal structure. Indeed, according to the thermodynamic stability diagram p_{O_2} *vs.* T [7], the growth conditions commonly used for YBaCuO thin film deposition (about 750°C at 0.3 mbar) correspond to an oxygen deficient phase, around $O_{6.1}$, with a tetragonal structure. Subsequently, in order to obtain fully oxygenated superconducting films with an orthorhombic structure, the oxygen uptake should occur, according to the thermodynamic stability diagram, during the sample cooling at high oxygen pressure (1 bar).

We have recently observed that depending on the sample cooling conditions (cooling rate, oxygen pressure), ~ 5000 Å thick YBaCuO films can exhibit either an orthorhombic or a quasi-tetragonal structure [6, 8]. The former is obtained by low cooling rates at high oxygen pressure (0.2–1 bar), whereas the latter needs high cooling rates (higher than 100°C/min), even at low oxygen pressures. Our oxygen content measurements show that both kinds of samples are fully oxygenated ($\sim O_7$) YBaCuO thin films with T_c onset of 91 K. In the present paper we describe a systematic investigation concerning the cooling procedure effects on the lattice parameters, crystal structure, and superconducting properties of ~ 5000 Å thick YBaCuO films deposited on $LaAlO_3$ single-crystal substrates. Also, the possibility of the existence of fully oxygenated (O_7) superconducting YBaCuO films with a tetragonal structure is discussed.

2. Thin film preparation

YBaCuO thin films were prepared *in situ* by inverted cylindrical magnetron sputtering of a stoichiometric $Y_1Ba_2Cu_3O_7$ target. The nominal O_7 oxygen composition of the target was checked by RBS and NRA measurements. The films were prepared according to a two-step procedure with a thickness of about 5000 Å. In the first step, the films were deposited on $LaAlO_3$ single-crystal substrates kept at 750°C. A mixture of Ar and O_2 was used with partial pressures of $p_{O_2} = p_{Ar} = 0.35$ mbar. In these conditions, it is generally assumed that the films grow in the oxygen deficient tetragonal phase and that a second step is necessary for the oxygen uptake, which leads to the orthorhombic structure [7]. All the films were cooled from the deposition temperature to 500°C very quickly, in about 2 minutes. In order to study the effect of the second step on the physical properties, we performed three kinds of cooling procedures from 500°C. In the first case, the samples referred to here after as A-films were cooled at high oxygen pressure (1 bar). This kind of films usually show good physical properties and therefore we will use them as a reference when comparing to the other samples. The other films were cooled at the deposition oxygen pressure (0.35 mbar), but whereas for the B-films the cooling rate was very slow (3°C/min), the C-films followed a rapid quenching to room temperature (90°C/min). We are interested on the behavior of the physical and structural properties of the films as a function of the oxygen cooling kinetics.

3. Experimental

3.1. X-ray diffraction

The a, b, c-axis lattice parameters of the superconducting YBaCuO thin films were determined at room temperature using a high-performance X-ray diffraction setup with a K_α copper radiation ($\lambda = 1.5405$ Å). While in the standard Bragg-Brentano (θ–2θ) geometry only lattice planes parallel to the surface substrate can be detected, we used an original configuration in order to measure both symmetrical and asymmetrical reflections. This new method, which will be discussed in a forthcoming paper, allows us to determine the a, b, c-axis lattice parameters simultaneously on the same kind of YBaCuO grains, whose c-axis is perpendicular to the sample surface. Assuming an orthorhombic unit-cell, a software program for calculating lattice parameters determines the set of a, b, c values which accomplish the best fit between calculated and experimental (hkl) diffraction values (2θ). Hence, from these parameters we can determine the crystal structure of the YBaCuO unit-cell and relate it to the oxygen content and the physical properties. For the three series of samples, a complete (θ–2θ) symmetrical scan, showing $(00l)$ reflections up to $l = 9$, and three asymmetrical reflections (108), (1010), (128), was recorded. The a, b, c-axis lattice parameters were calculated from experimental 2θ values of (007), (008), (009), (108), (1010), and (128) peak positions, determined automatically by the centroid of their second derivative. The absolute error on the a, b, c experimental values was less than 10^{-3} Å. The main purpose for using the asymmetrical reflections (108), (1010), (128), was to calculate the a, b, c-axis lattice parameters simultaneously on the same YBaCuO grain.

TABLE I. Characteristics of the 5000 Å thick YBaCuO films deposited on $LaAlO_3$ substrates.

sample	$T_c(R = 0)$ (K)	T_c(onset) (K)	ΔT_c (K)	ρ(300K) (mΩcm)	R_s (mΩ)
A	91.0	91.7	0.7	218	0.5
B	81.4	91.2	7.1	470	-
C	88.0	91.5	2.7	638	3.2

3.2. Thin film composition

The composition and the microstructure of the YBaCuO thin films were studied using IBA techniques [6]. Hence, Rutherford backscattering spectrometry (RBS), with a 2.2 MeV ^{4}He beam in random incidence, allows us to determine the cation (Y,Ba,Cu) stoichiometry. For the oxygen measurements, we used the elastic $^{16}O(\alpha, \alpha)^{16}O$ scattering resonance at 3.045 MeV [6]. Moreover, information on the quality of the crystalline structure of the films was obtained using RBS in channeling geometry. The minimum yield $\chi_{\min}$, which is the ratio of the yield for perfect alignment (channeling) to that of random incidence, is a measure of the quality of the crystalline structure. On the other hand, additional information concerning the kind of crystalline defects in the film structure can be obtained studying the variation of $\chi_{\min}$ as a function of the beam energy square root.

4. Results

4.1. Electrical properties

Table I shows the electrical properties for the three kinds of samples. The resistivity measurements $\rho(T)$ were performed by the standard four-point method. All the films presented very high critical transition temperatures T_c (onset). Take notice of the excellent properties of the A-film (cooled at 1 bar, according to the classical method), in particular the surface resistance R_s, measured at 77 K and 10 GHz, which is among the lowest values reported to date. This film will play for us the role of a reference. Compared with the other films, the transition width ΔT_c of the B-film is quite broad and for that reason the T_c at zero resistance is low. Moreover, the $\rho(T)$ curve (Fig. 1) for this film presents a shoulder (broader ΔT_c) and also R_s is too high for being measured. This indicates that the oxygenation within the film is both incomplete and not homogeneous, *i.e.*, even if the main part of the B-film is superconducting with a transition near 91 K, there is a small fraction with a T_c around 81 K. Indeed, the whole shape of the resistivity curves may be related to the YBaCuO crystalline structure and it is generally assumed that a linear temperature dependence of $\rho(T)$, with zero intercept, is a typical behavior of a conduction along perfectly ordered chains and an indication of the high quality of the crystalline structure [9]. This can be the case for the A-film.

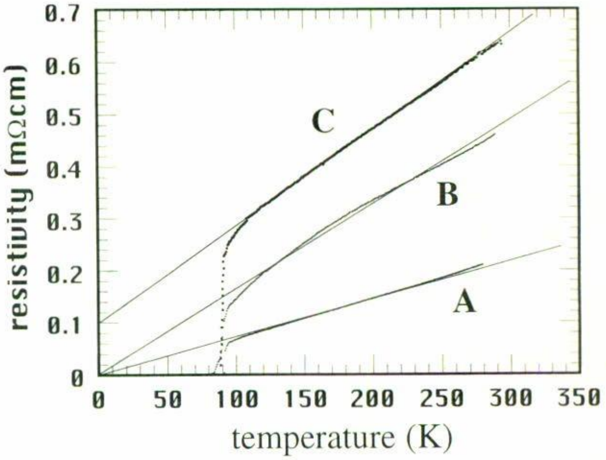

FIGURE 1. Resistivity curves $\rho(T)$ as a function of the temperature for the A, B, C-films deposited on $LaAlO_3$. Notice that in the case of the A-film the $\rho(T)$ curve has a linear dependence which extrapolates to zero intercept. Even for the slowly cooled B-film it is possible to fit the $\rho(T)$ curve as a straight line passing also through the origin. However, the quenched C-film shows a linear behavior that intersects the resistivity axis at a large positive value.

On the other hand, the quenched C-film presents a T_c unexpectedly higher than that of the slowly cooled B-film. Furthermore, the latter film shows a general degradation on their electrical properties compared with those of the quickly cooled C-film. Thus, it results that the film quality is negatively affected by the quite slow cooling rate at low oxygen pressure. In other words, accordingly to our oxygen content measurements (see below), it seems that during the *in situ* thin film deposition by cathodic sputtering, the oxygen content is actually higher than that expected from merely thermodynamical considerations [7]. Therefore, if this is the case, the YBaCuO film grows fully oxygenated and, in principle, the oxygen content must be rather retained by means of a rapid quenching, and it seems that the second preparation step is not completely necessary for the oxygen uptake.

4.2. Structural properties

The X-ray patterns exhibit mainly $(00l)$ peaks, proving that all the films were oriented with the c-axis perpendicular to the

TABLE II. The a, b, c-axis lattice parameters measured at room temperature and the $b-a$ difference for the 5000 Å thick YBaCuO films deposited on $LaAlO_3$ substrates and prepared following the three kinds of cooling procedures described in the text. The corresponding values for the orthorhombic $YBaCuO_7$ [10] and the tetragonal $YBaCuO_6$ [11] compounds are presented for comparison.

sample	p_{O_2}	a-axis (Å)	b-axis (Å)	c-axis (Å)	$b-a$ (Å)
A	1 bar (3°C/min)	3.854	3.878	11.691	0.024
B	0.35 mbar (3°C/min)	3.828	3.885	11.721	0.057
C	0.35mbar (90°C/min)	3.856	3.859	11.694	0.003
O_7	-	3.823	3.888	11.681	0.065
O_6	-	3.857	3.857	11.819	0.000

the substrate surface and that extra phases were not present. A quite a small fraction ($<$ 5%) of YBaCuO grains were oriented following the a-axis direction. This value was calculated from the intensities of the (005) and (200) diffraction peaks taking into consideration that $I(200) = 3I(005)$. Table II shows the a, b, c-axis lattice parameters corresponding to the 5000 Å thick YBaCuO films prepared according to the three kinds of cooling procedures described before. For comparison, the corresponding values for the orthorhombic $Y_1Ba_2Cu_3O_7$ [10] and the tetragonal $Y_1Ba_2Cu_3O_6$ [11] compounds are included. First that all, we must notice that the c-axis lattice parameter is essentially the same for both the A-film cooled at 1 bar and the rapid quenched C-film. In this case, as we will show below, the oxygen content is practically the same for both films. On the other hand, the B-film, slowly cooled at 0.35 mbar, shows a c-axis lattice parameter longer than those of the other films. This fact probably means that the oxygen content of the B-film is slightly lesser than those of the A and C-films and may explain also their poor electrical properties.

Our XRD measurements show that the slowly cooled B-film has an orthorhombic twinned structure, and the values of the a and b-axis lattice parameters are in agreement with those measured on fully oxygenated $Y_1Ba_2Cu_3O_7$ single-crystals. However, the B-film presents not only the longest c-axis lattice parameter, but their electrical properties are degraded. On the other hand, for the quenched C-film the a and b-axis lattice parameters would correspond to an unexpected quasi-tetragonal structure. Moreover, the c-axis lattice parameter is practically the same for this film and the A-film, which presents the best properties. As we established before, the lattice parameters were determined as the set of a, b, c values which accomplish the best fit between calculated and experimental (hkl) diffraction values (2θ). In this case, according to our results, it seems that we are dealing with a fully oxygenated (O_7) superconducting film with a quasi-tetragonal structure.

One explanation may be that this quasi-tetragonal structure can be due to the formation of very little orthorhombic domains (of about several hundreds of Å), which can not be discerned by our XRD setup and are aligned along the a-axis direction as well as along the b-axis direction. While oriented along both the a and b axes, the average symmetry of the system may be macroscopically tetragonal, but the local symmetry remains orthorhombic because ordered Cu-O chains still exist on a local site. Another possibility is the existence of a fully ordered microscopic tetragonal structure, as found for the $LaBa(Ca,Sr)Cu_3O_{7-x}$ compound [12]. This structure consists of a full-empty-full sequence of Cu-O chains running along both the a and b axes, which leads to an oxygen content O_7. Recently, theoretical electronic-structure calculations showed that the hole density in this microscopically ordered tetragonal structure is practically identical to that found in the orthorhombic phase [13]. In this case, the critical temperature T_c would be the same for both orthorhombic and tetragonal ordered structures. The question is to establish whether the microstructure of this kind of films is actually tetragonal at the scale of the YBaCuO unit-cell or it is a quasi-tetragonal one, composed of small domains having locally an orthorhombic symmetry. To answer to this question, we have performed a quite complete transmission electron microscopy (TEM) study concerning the crystallographic structure of the samples as a function of the cooling conditions. Here, only a short summary of the main results is presented because the related paper was recently published [14]. Hence, the rapid cooled samples showed the presence of a superconducting (O_7) tetragonal phase, which is not ordered and where unrelaxed lattice strains were revealed by the curvature of the lattice planes. It means that this kind of films show a mixed phase structure (orthorhombic + tetragonal), where the tetragonal structure is dominant. On the other hand, the slowly cooled films exhibit a dominant orthorhombic structure [14].

Moreover, the resistivity curve of the quenched C-film (Fig. 1) shows some particular features that are similar to those observed in the case of the $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})Cu_3O_{7-x}$ compound, which belongs to the 1-2-3 family and presents a tetragonal structure [9]. Indeed, in both cases the resistivity is higher than that observed in the orthorhombic YBaCuO compound and the $\rho(T)$ curve has a linear dependence, extrapolating to a non-zero intercept. All these features suggest that the fully oxygenated quasi-tetragonal structure would be preserved by a rapid quenching to room temperature at low oxygen pressure.

4.3. Oxygen composition and channeling studies

The composition of the three series of films was determined by RBS with a 2.2 MeV ^{4}He beam and by the elastic $^{16}O(\alpha, \alpha)^{16}O$ scattering resonance at 3.045 MeV [6]. Our results show that the oxygen content is practically the same for both the A-film, slowly cooled at an oxygen pressure of

1 bar and the C-film, quenched at 0.35 mbar. This result is in agreement with the fact that both films have also the same c-axis lattice parameter. On the other hand, according to the precision of our measurements, we can not confirm if the oxygen content of the B-film, slowly cooled at 0.35 mbar, is lesser than those of A and C-films. However, the poor physical properties of the B-film, together with its enlarged c-axis lattice parameter, seem to indicate that its oxygen content is slightly lesser than those of A and C-films. Moreover, the presence of a shoulder around 85 K in the $\rho(T)$ curve indicates that the oxygenation of the B-film is not completely homogeneous (Fig. 1). In any case, the absolute oxygen composition corresponding to the 1-2-3 phase is $O_{6.9\pm0.1}$ for the three films.

For explaining the full oxygenation (O_7) of the quenched C-film and the deterioration of the physical properties of the slowly cooled B-film, one may to admit that the whole oxygenation (O_7) occurs indeed during the *in situ* film growth. The high oxygenation obtained during the film deposition is not far from the O_7 oxygen composition and is probably due to the presence of atomic oxygen in the sputtering plasma [8]. On the other hand, our XRD and TEM structural studies show that the quenched C-film presents mainly a quasi-tetragonal structure. Therefore, according to our results, we can assume that the YBaCuO thin films grow with a tetragonal structure and with an oxygen content (O_7) higher than that expected from merely thermodynamical considerations ($O_{6.1}$) [7]. These features can be preserved if the film is rapidly quenched to room temperature at low oxygen pressure, leading to the formation of a not ordered quasi-tetragonal phase with a high critical temperature ($T_c \sim 90$ K), comparable with that observed in the case of fully oxygenated films with an orthorhombic structure. However, it seems that the classical second preparation step, *i.e.*, the slow cooling at high oxygen pressure, is important for increasing the order in the oxygen sublattice [15]. Moreover, we have also obtained superconducting YBaCuO films after a fast cooling in a pure Ar atmosphere (*i.e.*, without post-oxygenation). These films were well oxygenated and presented $T_c > 85$ K. Our results will be published in a forthcoming paper, but similar results were reported by others groups cooling their samples in nitrogen [16].

In order to study the structural quality of our films using IBA techniques, we have determined the $\chi_{\min}$(Ba) value with a 2.2 MeV ^{4}He beam in channeling geometry. It was found that the $\chi_{\min}$(Ba) value were 3.2%, 18% and 15% for the A, B and C-film, respectively. These results show that whereas the A-film crystallinity is very high, the B and C-films present some structural disorder in the Ba lattice. Moreover, additional information about the crystalline defects in the films was obtained by performing the channeling studies at three different energies: 0.55, 1.1 and 2.2 MeV. Figure 2 shows the $\chi_{\min}$(Ba) curves as a function of the ^{4}He beam energy square root for the three $\sim$ 5000 Å thick YBaCuO films deposited on $LaAlO_3$ substrates. According to these results, two well defined behaviors are observed. The $\chi_{\min}$(Ba) remains constant, independently of the beam energy, for both the A-film cooled 1 bar and the slowly cooled B-film, both ofthem presenting a dominant orthorhombic structure. In contrast, in the case of the quenched C-film, having a quasi-tetragonal structure, the $\chi_{\min}$(Ba) increases linearly with the beam energy square root.

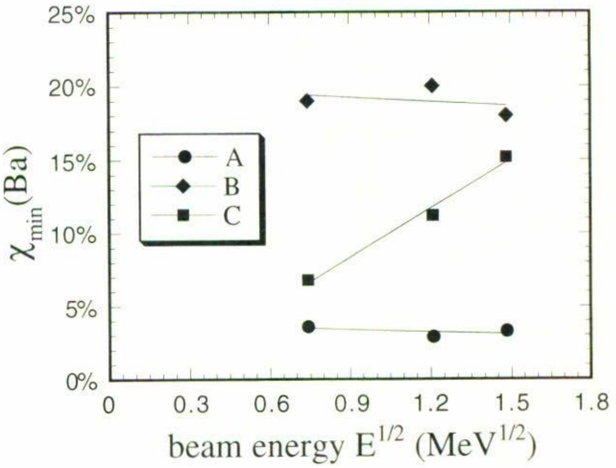

FIGURE 2. $\chi_{\min}$(Ba) curves as a function of the ^{4}He beam energy square root for the three kind of 5000 Å thick YBaCuO films deposited on $LaAlO_3$ substrates.

A beam energy independent $\chi_{\min}$ value indicates that the film contains some small polycrystalline fractions or stacking fault defects, whereas a linear dependence of $\chi_{\min}$ with the beam energy reveals the presence of extended defects, such as dislocations [17]. On the other hand, in contrast with single-crystals or polycrystalline material, thin films are deposited on substrates and, in this case, there is always a lattice mismatch between the YBaCuO film and the substrate. This mismatch usually induces some lattice strains between the film and the substrate and must be taken into consideration. Most of the films grow in better crystallinity with the increase of the film thickness, reflecting the relaxation of the lattice mismatch with the substrate. It should be noted that the $\chi_{\min}$ determination corresponds just to the first hundreds of angstroms from the film surface. This suggest that the 5000 Å thick A and B-films probably contain, near the film surface, some micro-structural defects such as stacking faults, polycrystalline precipitates or an extremely low dislocation density. According to this, we consider that, likely owing to an extremely high dislocation density near the film-substrate interface, these films could release their internal strains. Therefore, they grow without strains and the bulk of the film is relaxed, leading systematically to the orthorhombic structure.

In contrast with these samples, the quasi-tetragonal C-film, quenched at 0.35 mbar, systematically contains dislocations within the film, even in the near surface region. This means that while the dislocation density near the film-substrate interface is too low for release the internal strains, it is enough for increasing the ion dechanneling with the beam energy. The origin of this dechanneling may be explained by the fact that the path of an energetic ion will be perturbed by crossing over near a dislocation defect or by a strained lattice [17]. Moreover, these unrelaxed strains were actually revealed by the curvature of the lattice planes [14]. Therefore, we consider that these systematic trends, such as the crystal structure (studied by XRD and TEM), and the resistivity $\rho(T)$ and $\chi_{\min}(\mathrm{Ba})$ behaviors, provide more insights about the possible existence of fully oxygenated (O_7) superconducting YBaCuO films with a quasi-tetragonal structure.

5. Conclusions

We have shown that YBaCuO films cooled at low oxygen pressure have almost the same oxygen content than those cooled at high pressure. Moreover, we found that the cooling rate affects the physical properties and the oxygen content of the films cooled at low pressure. Hence, if films are cooled at low oxygen pressures, the best properties are observed in the films quickly cooled to room temperature. Our results allow us to conclude, in opposition to the well admitted thermodynamical model, that the full oxigenation of the YBaCuO films takes place during the *in situ* high temperature growth by cathodic sputtering and not during the cooling procedure. We explain this effect by the presence of oxygen activated species (*i.e.*, atomic oxygen), which enhance the film oxygenation during the growth by sputtering deposition. This means that thin film growing mechanism does not occur in thermodynamic equilibrium conditions.

On the other hand, the films quickly cooled at low oxygen pressure are superconducting and present a quasi-tetragonal crystal symmetry. Therefore, it seems that the YBaCuO films actually grow with a high oxygen content, near of O_7, and with a tetragonal structure and these features can be preserved by means of a rapid quenching to room temperature at low oxygen pressure. We showed by TEM [14] that both the orthorhombic and the tetragonal phases coexist in the same film and, in this case, the relative abundance of each phase depends on the cooling rate. While a rapid quenching to room temperature seems to preserve the tetragonal structure, a slow cooling rate promotes the transition to the orthorhombic one.

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