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Study of oxygen content and of disorder in YBaCuO thin films with enlarged c-axis lattice parameter *

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Abstract

It was recently shown that YBaCuO thin films prepared at low oxygen partial pressure p_{O2} present enlarged c-axis lattice parameter. In this paper, we report on further results concerning the c-axis expansion effect, but on films produced at particular conditions: they were deposited at relatively high p_{O2} = 0.25 mbar and then cooled to RT at the same oxygen partial pressure. A question arises: are these films fully oxidized or are they oxygen deficient films, according to the relationship between the c-axis parameter and the oxygen content? YBaCuO thin films were deposited, on MgO single crystal heated to about 750°C, by inverted cylindrical magnetron sputtering of a stoichiometric $Y_1Ba_2Cu_3O_7$ target, at an oxygen partial pressure p_{O2} = 0.25 mbar. A series of samples was cooled down to room temperature at the same pressure (0.25 mbar) and a second one, at higher pressure (1 atm). As grown samples were characterized by ρ(T) resistivity measurements (T_c, ΔT_c). Their composition and structure were studied by Rutherford Backscattering Spectrometry (RBS) in random and channeling geometries, Nuclear Reaction Analysis (NRA), X-ray Diffraction (XRD) and Raman Spectroscopy. The oxygen contents, measured by RBS and NRA, were compared to those deduced from XRD (c-axis parameter). A good agreement was found for the YBaCuO films cooled at 1 atm, but significantly higher results were obtained by RBS and NRA for the films cooled at 0.25 mbar. These results suggest that the cooling at low oxygen partial pressure leads to the formation of films with enlarged c-axis parameter, but with T_c values similar to those observed for the samples cooled at p_{O2} = 1 atm ($T_c \approx 88$ K). The results are discussed.

1. Introduction

The superconducting properties of high T_c $Y_1Ba_2Cu_3O_{7-\delta}$ material depend not only on the oxygen content, but also on the presence of structural defects and their ordering [1]. The critical transition temperature T_c is a sensitive function of the deviation from the oxygen stoichiometry and of the ordering of the oxygen vacancies in the CuO chain-planes. Moreover, in the case of single-crystal or bulk poly-crystalline YBaCuO samples, there is a direct correlation between the c-axis lattice parameter and the oxygen content. Often, the oxygen stoichiometry is deduced from the c-axis parameter measured by X-ray diffraction (XRD) [2,3,4]. However, for YBaCuO thin films deposited at low oxygen partial pressure, the above relation does not hold, because of the anomalous expansion of the c-axis parameter [5]. Moreover, we have observed a similar effect even in the case of films deposited at relatively high oxygen partial pressure (p_{O2} = 0.25 mbar) and cooled down to room temperature (RT) at the same pressure [6]. Indeed, we found that films having quite good superconducting properties ($T_c \approx 88$ K) present enlarged c-axis lattice parameter, which would correspond to oxygen deficient films.

The aim of this paper is to present further results concerning the c-axis parameter expansion. We have studied this effect on YBaCuO thin films deposited, by inverted cylindrical magnetron sputtering, on MgO single crystal heated at about 750°C at an oxygen partial pressure of 0.25 mbar. The cooling process was performed either at low (0.25 mbar) or at high (1 atm) oxygen partial pressure. The oxygen content was determined by Ion Beam Analysis (IBA) techniques, using Nuclear Reaction Analysis (NRA) and Rutherford Backscattering Spectrometry (RBS) and the results were compared with those deduced from the c-axis parameter measured by XRD. In addition, YBaCuO films were annealed in $^{18}O_2$ in order to perform the total $^{18}O \rightarrow {}^{16}O$ exchange, to measure the ^{18}O content and to evaluate the precision of our RBS results. On the other hand, an $^{16}O_2$ annealing followed by a quenching allows us to obtain oxygen deficient films, which can be used to compare RBS and XRD oxygen measurements.

2. Thin film preparation and characterization

YBaCuO thin films, with a thickness ranging from 800 to 4000 Å, were prepared by inverted cylindrical magnetron sputtering of a stoichiometric $Y_1Ba_2Cu_3O_7$ target, by a two-step procedure. In the first step, the films were deposited on single crystalline MgO (100) substrates,

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kept at about 750°C. A mixture of Ar and O_2 was used with partial pressures of $p_{O2} = p_{Ar} = 0.25$ mbar. In these conditions, the films grow in the tetragonal phase and a second step is necessary for the oxygen uptake, leading to the orthorhombic superconducting structure. In order to prepare YBaCuO films with different oxygen contents, we performed two kinds of second step procedures. On the one hand, for the (i)-films, the oxygen uptake was achieved by cooling the samples slowly from the formation temperature (750°C) to RT, at the same oxygen partial pressure (0.25 mbar). On the other hand, for the (ii)-films, the cooling to RT was carried out at 1 atm [7]. In these conditions, we expected the latter samples to be more oxygenated that the former ones.

2.1. Annealing conditions

We have recently shown [8] that the annealing in $^{18}O_2$ atmosphere at 650°C during 19 hours at an oxygen partial pressure of $p_{O2} = 200$ mbar, allows the total $^{18}O \rightarrow {}^{16}O$ isotopic exchange. From the thermodynamical stability diagram of oxygen partial pressure versus temperature, these conditions correspond to an oxygen stoichiometry of about $O_{6.6}$. In order to have fully oxygenated films, the furnace has been switched off for a slow cooling from 650°C to RT at the same oxygen partial pressure. The experiments were carried out in a furnace built in UHV technology (base pressure 10^{-9} Torr) allowing annealings in dry oxygen. All the annealings were performed in the same conditions: a temperature of 650°C and an oxygen partial pressure of 200 mbar, during 19 hours, but the time required for the cooling to room temperature was different: B-samples: annealing in $^{18}O_2$, after which the furnace was switched off for a slow cooling to RT in about 6 hours and C-samples: annealing in $^{16}O_2$, fast quenching in a few minutes.

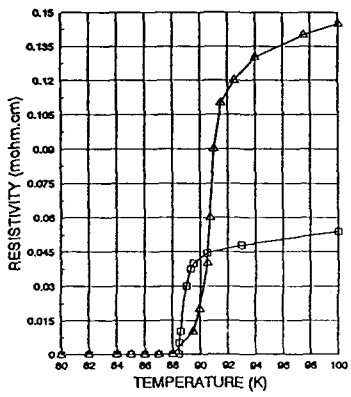

Fig.1. Temperature dependent resistivity ρ(T) for the as-prepared (i) and (ii)-films (▲ and ■, respectively).

3. Experimental and results

3.1. Resistivity measurements ρ(T)

The resistivity measurements ρ(T) were performed by the standard four-point method. Fig. 1 shows the resistivity as a function of the temperature for the as-prepared (i) and (ii)-films. Unexpectedly, all the films presented nearly the same critical transition temperature $T_c \approx 88$ K, independently of the second step oxygen uptake procedure. However, the transition width ΔT_c and the film resistivity at 300 K seem to depend significantly on the second step oxygen partial pressure. While the (i)-films presented broader ΔT_c and higher resistivity values than those corresponding to the (ii)-films, the resistivity curves dropped down to the same critical transition temperature [6].

3.2. X-ray diffraction

The crystallographic unit cell c-axis parameter is related to the oxygen content in single-crystal or bulk poly-crystalline material [3,4]. In this case, the oxygen composition is easily deduced from the c-axis parameter. However, for thin films, this relationship is actually contested: the expansion of the c-axis parameter would be induced by a low oxygen partial pressure during the very film deposition and would not be explained only by oxygen deficit in the Cu-O chains [5]. To study this effect, some of our YBaCuO films were cooled at relatively low oxygen partial pressure. The c-axis parameter was measured by XRD, using the radiation coming from a copper X-ray tube in the Bragg-Brentano geometry. In this configuration, only lattice planes parallel to the MgO substrate can be detected.

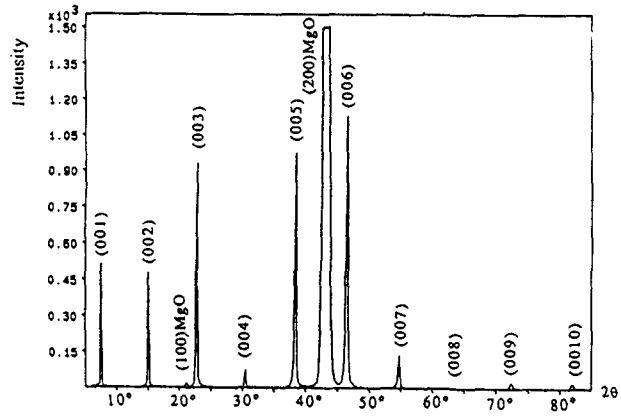

Fig.2. X-ray diffraction patterns for the (i)-films.

As shown in Fig. 2, X-ray patterns for the (i)-films exhibit only (00*l*) peaks, proving that all the films were oriented with the c-axis perpendicular to the substrate surface and that extra phases was not present. A similar pattern is obtained for the (ii)-films (not shown). A large difference was observed in the value of the c-axis parameter: 11.74 and 11.70 Å for the (i) and (ii)-films, respectively. The precision on the value of the c-axis parameter is about 0.01 Å. Deduced from the c-axis parameter analysis, the oxygen composition of the films would range from $O_{6.56}$ to $O_{6.9}$ [4]. The results show that (i)-films would be oxygen deficient films, whereas (ii)-films would be fully oxygenated. Nevertheless, it must be noted that the critical transition temperature T_c is practically the same for all the samples, independently of the c-axis value. So there is an inconsistency between the oxygen stoichiometry deduced from the c-axis

measurements and the observed T_c's, in the case of the (i)-films, cooled at relatively low oxygen partial pressure (0.25 mbar). Moreover, a significant difference was observed between the XRD spectra recorded on the (i) and (ii)-films concerning the intensity ratio of peaks 001 over 002. Fig. 2 shows that this ratio is higher than 1 for (i)-film, whereas for (ii)-film this ratio is inversed (not shown). Note that theoretical calculations [9] are in qualitative agreement with the results obtained on the (ii)-sample.

3.3. RBS measurements

The 2.5 MV single ended Van de Graaff accelerator of the Groupe de Physique des Solides was used in order to measure by IBA techniques the composition of the YBaCuO films. The cation (Y,Ba,Cu) and the oxygen stoichiometries were determined by RBS with a 2.2 MeV ^{4}He beam, in random geometry. For all the samples, the cation stoichiometry was close to the 1-2-3 ratio.

In order to find the oxygen stoichiometry we used the RUMP program [10] for RBS simulations. Once well evaluated the experimental parameters (solid angle, dose) and the cation stoichiometry, the fit is obtained by varying only the oxygen composition [11]. As an example, Fig. 3 presents the experimental RBS spectrum in random geometry and the corresponding RUMP simulation for the ^{18}O annealed sample. The precision on the oxygen stoichiometry so determined is about $O_{x\pm0.15}$. If we plot the simulated RBS spectra corresponding to oxygen compositions of $O_{x-0.15}$ and $O_{x+0.15}$, one can verify that in both cases, the fits are not good enough. For the (i)-films, supposed to be oxygen deficient according to the relationship between the c-axis parameter and the oxygen stoichiometry, the oxygen content deduced from RBS is not less than $O_{6.8}$. While showing enlarged c-axis parameters (11.73 - 11.74 Å), this films presented quite good critical transition temperature ($T_c \approx 88$ K). Therefore, the RBS results are more consistent with the superconducting properties (T_c) that the XRD ones (c-axis parameter).

3.4. NRA ^{18}O measurements

Oxygen content measurements of YBaCuO thin films by NRA are limited by the fact that oxygen is also present in the substrate (MgO). An indirect way to determine the oxygen stoichiometry is to carry out the total exchange of the ^{16}O in the as-prepared samples by the ^{18}O isotope and to measure the latter using the selective ^{18}O(p, α)^{15}N nuclear reaction at 730 keV. The absolute ^{18}O contents so measured are in agreement with the absolute ^{16}O contents deduced from RBS simulations on the as-prepared A-samples. The precision of these results is about 4% [6].

In addition, we performed RBS measurements with a 2.2 MeV ^{4}He beam on the ^{18}O annealed B-samples in order to compare the ^{18}O contents deduced from RBS with our previous NRA ^{18}O results. The ^{18}O stoichiometry was determined using the RUMP simulation program. According to the precision of our measurements, we have found, on the one hand, the same absolute oxygen content calculated by RUMP for the samples A and B and, on the other hand, a good agreement between RUMP calculations and direct ^{18}O measurements by NRA. While from RBS and NRA measurements, the A and B-samples have practically the same oxygen stoichiometry, this one is significantly higher than that deduced from XRD in the case of the (i)-samples, corroborating the expansion of the c-axis parameter. Because of the fact that our IBA results show that all the films are fully oxygenated (at least $O_{6.8}$), the c-axis expansion effect can not be explained by an oxygen deficit in the CuO chain-planes. It must be noted that the difference in the c-axis parameter between the (i) and (ii)-films probably arises from the use of different oxygen partial pressures during the cooling process and not from the use of low oxygen partial pressure during the deposition as was reported elsewhere [5].

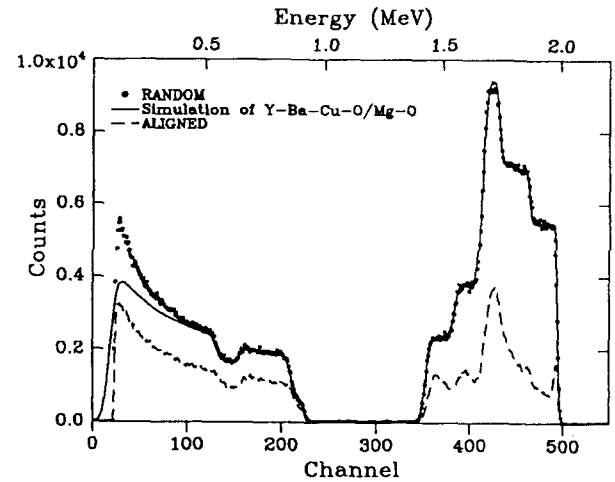

Fig.3. Aligned, random and simulated 2.2 MeV ^{4}He RBS spectra for the as-prepared (ii)-film ($Y_1Ba_{1.85}Cu_{2.85}O_{6.9}$).

3.5. NRA ^{16}O measurements

An alternative NRA technique to measure the oxygen content of YBaCuO films and to avoid the detection of the oxygen coming from the substrate is to use the ^{16}O(^{3}He, α)^{15}O nuclear reaction. Detecting at $\theta = 90°$, the cross section of this reaction present a strong peak at about 2380 keV and a drastic reduction below 2 MeV [12]. When the films are not thick enough, the substrate contribution can be minimized if the samples are tilted, in order to increase the path traversed by the incident ^{3}He ions through the YBaCuO film. For a given film thickness, our experimental setup allows us to use large enough tilt angles and in this case we found that the measured α-yield shows a saturation effect. This means that the energy lost by the ^{3}He ions is large enough to decrease the nuclear reaction cross section and to minimize the substrate contribution. In order to determine the oxygen stoichiometry, the use of a NRA simulation program (SENRAS) is necessary because of the cross section variations [13].

Fig. 4 shows the α-yield curves calculated, for different oxygen contents, by the SENRAS program as a function of the tilt angle. The simulations show a saturation effect for tilt angles above 80°, for a 4000 Å thick YBaCuO/MgO film. The parameters involved in the

calculations correspond to the conditions of the experiment: we used the $^{16}O(^3He, \alpha)^{15}O$ reaction at 2420 keV (40 keV above the resonance energy) and a detecting angle of $\theta = 90°$. For tilt angles above 80°, the oxygen stoichiometry of the sample was determined evaluating its α-yield with respect to that corresponding to a stoichiometric $Y_1Ba_2Cu_3O_7$ film used as a reference. For good enough statistics, we can measure the oxygen composition with a precision better than $O_{x\pm0.1}$. For the 4000 Å thick YBaCuO film, we found that the oxygen stoichiometry of the $^{16}O_2$ annealed and then quenched C-sample differs by 0.4 ± 0.1 with respect to the fully oxygenated as-prepared A-sample, i.e., $O_{6.4}$ and $O_{6.8}$, respectively. The same samples were analized by XRD and their oxygen stoichiometries so measured differ by about 0.3. It must be noted that in this case, the oxygen composition deduced from XRD analysis is in agreement with the IBA results for the C-sample.

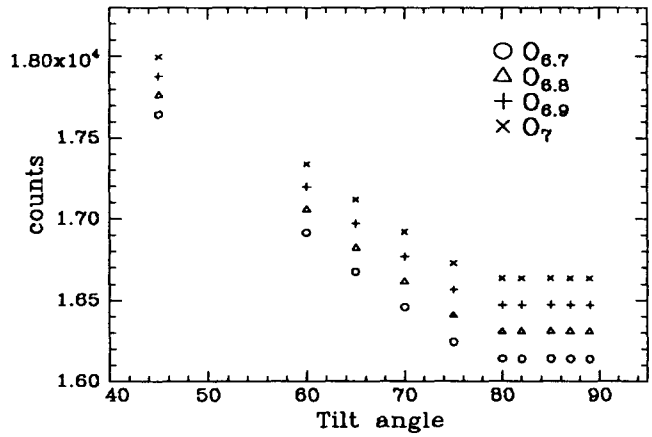

Fig.4. Calculated α-yield curves as a function of the tilt angle, using the $^{16}O(^3He, \alpha)^{15}O$ nuclear reaction, for a 4000 Å thick $Y_1Ba_{1.85}Cu_{2.85}O_x$ film, deposited on MgO, for different oxygen stoichiometries.

3.6. Microstructure analysis

Information on the quality of the crystalline structure of the films was obtained using RBS in channeling geometry with a 2.2 MeV ^4He beam. The minimum yield χ_{min}, which is the ratio of the yield for perfect alignment (channeling) to that of random incidence, showed that the as-prepared samples presented good crystalline structure. The (ii)-films showed a minimum yield in the Ba sublattice of $\chi_{min} \approx 8$ %, whereas for the (i)-films $\chi_{min} \approx 12$ %. Some of the samples were studied by Raman spectroscopy. No significant differences were observed between the samples cooled at 0.25 mbar and those cooled at 1 atm.

3.7. Effect of annealing

The significant differences on the electrical properties ($\rho(T)$, ΔT_c) between the as-prepared (i) and (ii)-films is preserved even after an annealing at $T \leq 500°C$ and $p_{O2} = 1$ atm. The long temperature annealing in $^{18}O_2$ and $^{16}O_2$ atmospheres at 650°C and 200 mbar supressed the differences between the (i) and (ii)-samples [6]. The physical implications of these results will be discussed in a next paper.

4. Concluding remarks

The oxygen stoichiometry determined by IBA methods is consistent with T_c measurements and show that all the films were well oxygenated, independently of the cooling process. The IBA results are in agreement with the XRD ones (c-axis parameter) only for the (ii)-films cooled at high oxygen partial pressure, but not for the (i)-samples cooled at low pressure. Indeed, the (i)-films exhibit enlarged c-axis parameter with respect to the corresponding values for single-crystal or bulk material, for a given stoichiometry. This effect may arise from the fact that the (i)-films presented some structural defects consisting in O(4) apical oxygen vacancies or to the presence of some stresses. Note that the tetragonal-orthorhombic phase transition takes place at 450 and 670°C, for (i) and (ii)-films, respectively. The origin of the c-axis expansion is studied.

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