Selective ^{18}O labelling in a-axis oriented YBaCuO thin films *

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Abstract

Superconducting YBaCuO thin films were deposited on $SrTiO_3$ substrate by inverted cylindrical magnetron sputtering of a stoichiometric target. The composition and the structure of the films were studied by Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA), in random and channeling geometries. Annealing treatments, allowing the selective $^{18}O \rightarrow {}^{16}O$ exchange in the CuO chain-planes, were performed in $^{18}O_2$ atmosphere. In order to accelerate the oxygen diffusion during the annealing, we used, on the one hand, a-axis oriented films and, on the other hand, we adopted thermodynamical conditions corresponding to an oxygen composition of $O_{6.6}$ ($p_{O2} = 0.13$ mbar and T = 400°C). The full oxygenation was accomplished by increasing the oxygen partial pressure to $p_{O2} = 200$ mbar at T = 400°C, during 30 minutes. The absolute ^{18}O content, determined by NRA, showed a partial and a non uniform $^{18}O \rightarrow {}^{16}O$ exchange. In spite of the fact that the RBS spectra were identical for different points on the sample, the NRA results confirmed that the absolute ^{18}O content varies from point to point. Moreover, Raman spectroscopy revealed some inhomogeneities concerning the oxygen site occupation by the ^{18}O tracer atoms in the YBaCuO lattice: In the center of the sample, ^{18}O atoms are present only in the CuO chain-planes, whereas few mm away of the center, we found the ^{18}O atoms also in the CuO_2 planes. These results are discussed.

1. Introduction

The physical properties of superconducting YBaCuO thin films depend on the oxygen stoichiometry and on the ordering of the oxygen atoms. The oxygen ordering in CuO chain-planes as a function of the temperature and of the oxygen stoichiometry was studied recently using Monte Carlo simulation programs based on the Ising model [1]. Experimentally, the disorder in the oxygen sublattice can be studied by neutron diffraction, Raman spectroscopy and MeV ion channeling using the nuclear resonance $^{16}O(\alpha,\alpha)^{16}O$ at 3.045 MeV. The latter two techniques are being used to study the defects in epitaxially grown YBaCuO thin films [2,3]. While the data obtained by Raman spectroscopy are not clear and need further studies, the results obtained by channeling are surprising [2]. Apparently, a huge disorder exists in the oxygen sublattice at least in the first 50 nm surface layer, as may be deduced from the analysis of the channeling spectra. The $^{16}O(\alpha,\alpha)^{16}O$ resonance in random and channeling geometries allows us to study the defects in the oxygen sublattice but it can not localize them. The aim of

this paper is to study experimentally the selective ^{18}O labelling of the CuO chain-planes in YBaCuO thin films. We combine NRA and Raman Spectroscopy, in order to measure and localize the ^{18}O atoms. On the other hand, the defects in the oxygen sublattice, particularly in the CuO chain-planes are studied using the selective nuclear reaction resonances: $^{16}O(\alpha,\alpha)^{16}O$ and $^{18}O(p,\alpha)^{15}N$ at 3.045 and 0.629 MeV respectively and these results will be published in a next paper.

2. Experimental

YBaCuO thin films with a thickness ranging from 150 to 550 nm were prepared by inverted cylindrical magnetron sputtering of a stoichiometric $Y_1Ba_2Cu_3O_7$ target by a two-step procedure. In a first step, the films were deposited on single crystalline $SrTiO_3$ (100) substrate, kept at about 650°C, followed by a second step in which the substrate temperature was increased to about 750°C. A mixture of argon and oxygen was used with partial pressure of $p_{O2} = p_{Ar} = 0.25$ mbar. The samples were cooled down to room temperature at $p_{O2} = 1$ atm. In this conditions, the films were a-axis oriented, growing with the c-axis parallel to the substrate surface [4]. The samples were also characterized by $\rho(T)$ resistivity measurements

performed by the standard four point method. RBS and NRA experiments were carried out with the 2.5 and the 3.75 MeV Van de Graaff accelerators of the Paris University and of the Kernforschungszentrum at Karlsruhe, respectively. The composition of the samples was determined by RBS with a 2.2 MeV $^4He^+$ beam and near the $^{16}O(\alpha,\alpha)^{16}O$ resonance at 3.045 MeV [5]. The samples were analysed 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 $SrTiO_3$ substrate can be detected.

2.1. O^{18} labelling

In order to perform the selective ^{18}O labelling of the CuO chain-planes one must work at low temperature. The oxygen diffusion coefficient following the a(b)-axis is about 10^5-10^6 times higher than that following the c-axis [6]. So this temperature should be also sufficiently high in order to ensure a large enough exchange rate between the oxygen gas and the oxygen in YBaCuO films. In a previous paper [7], we have shown that the annealing in $^{18}O_2$ atmosphere during 19 hours at $350°C$ and p_{O2}=200 mbar of c-axis oriented films is controlled by bulk diffusion which leads to a relatively small bulk labelling.

In order to increase the oxygen self diffusion coefficient (I_{sd}) in the bulk, we have used a-axis oriented films, increased the annealing temperature to $400°C$ and performed the annealing experiments at an oxygen partial pressure of $p_{O2} = 0.13$ mbar. At these conditions of temperature and pressure, the oxygen content of YBaCuO films corresponds to $O_{6.6}$ [8] and I_{sd} is about 20 times higher than in the case of O_7 [9]. As was shown in a previous study [7], the oxygen losses leading to the transformation of $Y_1Ba_2Cu_3O_7$ to $Y_1Ba_2Cu_3O_{6.6}$ takes place in about 5 minutes at $400°C$. On the basis of thermodynamics (stability of the orthorhombic phase) and kinetics considerations, we have chosen the following conditions for the ^{18}O labelling experiments. The annealing in $^{18}O_2$ gas enriched to 96% at $400°C$ and p_{O2} = 0.13 mbar, during 130 minutes, followed by 30 minutes at p_{O2} = 200 mbar. The annealing at 200 mbar leads to full reoxidation, restoring the $Y_1Ba_2Cu_3O_7$ stoichiometry. The experiments were performed in a furnace built in UHV technology allowing the annealings in dry oxygen [7].

The ^{18}O contents of the samples were measured using the $^{18}O(p,\alpha)^{15}N$ nuclear reaction at 730 keV. The ^{18}O profiles were determined using the $^{18}O(p,\alpha)^{15}N$ nuclear resonance at 629 keV [7]. Both measurements were performed in random geometry. The precision of this method is discussed in [10].

The ^{18}O substitution was measured by Raman spectroscopy using the U 1000 Jobin-Yvon double monochromator. A 180° backscattering geometry was used allowing the studies in Z(X, X+Y)Z geometry (the electric field E is always parallel to the sample surface). An argon laser was used (λ = 5145.2 Å), with a laser spot diameter of ≈ 1 μm and with a power density < 10 mW/cm^2. At these conditions the penetration depth is about 100 nm. Five vibrational modes are particularly interesting in this

study: 115 and 148 cm^{-1} corresponding to vibrations of Ba and Cu atoms, respectively; 338, 438 and 500 cm^{-1} characterizing oxygen vibration modes: O(3)-O(2) in-out phase motion; O(3)-O(2) in phase motion; O(4) vertical displacements, respectively [11]. Fig.1 presents schematically the different oxygen sites in the YBaCuO unit cell and their Raman identifications.
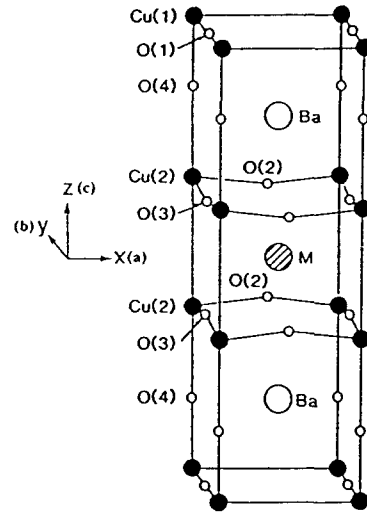

Fig.1. The unit cell of $Y_1Ba_2Cu_3O_7$ showing the atomic designation [11].

3. Results and discussion

In this paper we describe the results obtained on three YBaCuO samples prepared at the same conditions. All the samples were characterized by $\rho(T)$ resistivity measurements, XRD and Raman spectroscopy. One of them, the (i)-sample was used to determine by RBS and NRA the metallic and the oxygen compositions before the annealing treatments. The (ii)-sample was annealed in $^{18}O_2$ atmosphere as described above and the (iii)-sample was annealed at the same conditions but in $^{16}O_2$ atmosphere.

3.1. As prepared samples

The resistivity of the samples (T = 300 K) ranged from 2 to 5 $m\Omega cm$ for 150 and 550 nm thick films, respectively. The critical transition temperature was similar for all the films T_c ≈ 74 K (ρ=0) with ΔT ≈ 10 K. By XRD it was found that the films were a-axis aligned and that the volume of the material with the c-axis perpendicular to the substrate is lower than 1%. The Raman spectroscopy confirm these result. Moreover, the position of the Raman vibration mode of the O(4) apical oxygen at 500 cm^{-1} indicates that the samples are fully oxidized [11]. Therefore the relatively high value of resistivity and the poor T_c can not be explained only by low oxygen content of the as-prepared films.

Using the RUMP simulation program [12] for the RBS spectra measured in random geometry, it was

found that the composition of as-prepared (i)-sample is $Y_1Ba_{1.9}Cu_{2.9}O_7$ (Fig.2). The precision of these measurements is ± 0.05 for the metallic elements and ± 0.15 for the oxygen, as discuted in [5]. It was further confirmed that the composition of samples (ii) and (iii) is the same. From RBS measurements in random and channeling geometries the minimun yield value χ_{min} from 4.5 to 9 % was obtained for the Ba sublattice.
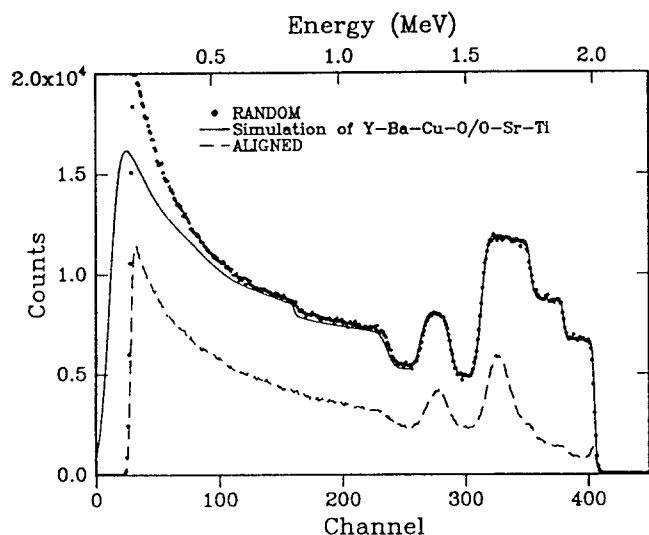

Fig.2. 2.2 MeV $^4He^+$ RBS spectra in random and aligned geometries recorded on as-prepared YBaCuO sample, deposited on the $SrTiO_3$ substrate. Simulated curve assuming $Y_1Ba_{1.9}Cu_{2.9}O_7$ composition (solid line).

Some experiments were also performed using the $^{16}O(\alpha,\alpha)^{16}O$ resonance at 3.045 MeV. A typical spectrum recorded at T ≈ 40 K is presented in Fig.3. Note that in this case the value of χ_{min} is 3.4% for the Ba sublattice and 23% for oxygen.
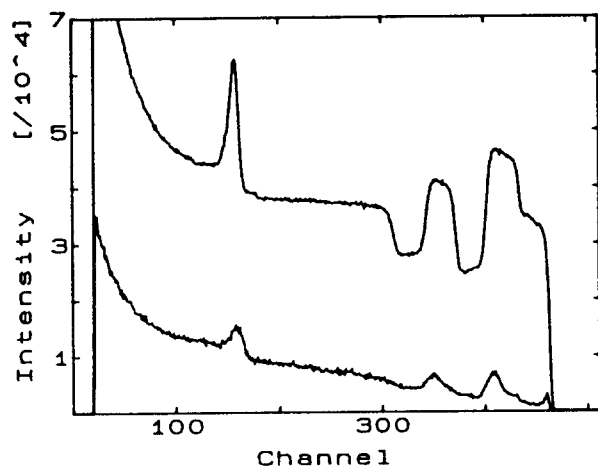

Fig.3. 3.045 MeV $^4He+$ RBS spectra in random and channeling geometries, recorded at T = 40 K on as-prepared YBaCuO sample deposited on the $SrTiO_3$ substrate.

3.2. Samples annealed in $^{18}O_2$ or $^{16}O_2$ atmospheres

A small degradation of resistivity and broadening of T_c transition was observed in annealed (ii) and (iii)-samples. The origin of this effect is unknown and needs further studies. In opposite to electrical properties, the Raman spectra for the (iii)-sample and the RBS spectra for both samples are similar to these found for the as-prepared (i)-sample. By RUMP simulation of the RBS spectra measured in random geometry it was found that the composition of (ii)-sample annealed in ^{18}O atmosphere is also $Y_1Ba_{1.9}Cu_{2.9}O_7$ and contains $(4000\pm200)10^{15}$ at/cm^2 (about 540 nm). Therefore the amount of oxygen atoms present in the chain-planes is equal to (315 ± 20) 10^{15} at/cm^2. By a similar calculation we found that 1260 10^{15} at/cm^2 of oxygen atoms are present in the CuO_2 planes and 630 10^{15} at/cm^2 in the BaO planes (O(4)).

3.3 Localization of ^{18}O atoms in YBaCuO structure by Raman spectroscopy and NRA

Fig.4 shows the Raman spectrum recorded at the center (a) and at the border (b) of the sample. Fig.4a is the same as recorded before the annealing treatment (not presented), i.e., there is not energy shift related to the ^{18}O annealing. This result could indicate either the absence of ^{18}O atoms in the center of the sample or the presence of ^{18}O atoms only in the chain-planes of the YBaCuO sample. In opposite to this result, the Fig.4b clearly shows the presence of the ^{18}O atoms in the CuO_2 planes and perhaps at the O(4) apical position. Let us recall that the Raman vibration modes are not sensitive to the ^{18}O labelling of the oxygen situated in the chain-planes [7]. The quantitative interpretation of these results is difficult to do without the knowledge of: (1°) the total ^{18}O content in the YBaCuO sample which is provided by NRA; (2°) the limit imposed by the Raman detection sensitivity to the ^{18}O labelling.

The total ^{18}O content of the sample was measured using the $^{18}O(p,\alpha)^{15}N$ nuclear reaction at 730 keV in random geometry. We found in the center of the sample: 260 10^{15} ^{18}O at/cm^2 and at the border 205 10^{15} at/cm^2. The precision of the measurements is about 4% [7]. The ^{18}O profile was determined by the $^{18}O(p,\alpha)^{15}N$ nuclear resonance at 629 keV and it was constant. The details of these measurements will be discussed in a separate paper. Therefore, the ^{18}O atoms present in the center of the sample are located only in the CuO chain-planes. It means that during the thermal annealing about 84% of the ^{16}O was replaced by the ^{18}O.

At present it is difficult to calculate quantitatively the distribution of the ^{18}O atoms among the different sites in the YBaCuO sample. It is believed that the presence of 3% of ^{18}O in the CuO_2 planes or at the O(4) position is the limit of Raman detection sensitivity (private communication). Note that 3% of ^{18}O in the CuO_2 planes and at the O(4) position corresponds in our sample to 60 10^{15} ^{18}O at/cm^2 which represents about 20% of the total ^{18}O content.

The situation is different at the border of the sample. A significant amount of the ^{18}O atoms present in

this part of the sample (205 10^{15} at/cm^2) is situated in the CuO$_2$ planes and perhaps at the O(4) position (Fig.4b). From the Raman spectrum a rough estimation of ^{18}O labelling in CuO$_2$ planes can be calculated. Note the presence of a second peak at 322 cm^{-1} corresponding to a shift of 17 cm^{-1}. We have recently shown [7] that the total ^{18}O labelling of the CuO$_2$ planes leads to a shift of 20 cm^{-1}. Assuming a linear relationship between the degree of ^{18}O labelling and the shift of the Raman peak at 339 cm^{-1}, part of the CuO$_2$ planes is labelled at 80% by the ^{18}O atoms. A question arises: How many of the CuO$_2$ planes are labelled at 80% by the ^{18}O? As the total amount of ^{18}O (205 10^{15} at/cm^2) corrected for 80% labelling represents about 20% of the total amount of oxygen present in the CuO$_2$ planes (1260 10^{15} at/cm^2), the upper limit is 20%. It is reasonable to assume that the ^{18}O labelling is also concerning the CuO chain-planes and perhaps the oxygen at the O(4) position. Therefore the amount of the CuO$_2$ planes labelled at 80% by the ^{18}O is obviously lower that 20% and probably situated about 10% (100 10^{15} at/cm^2). Note that the Raman peak at 500 cm^{-1} (FWHM) is much larger at the edge of the sample that at the center, indicating probably a small ^{18}O labelling. These results indicate that a significant part of YBaCuO unit cells located at the border of the sample contain some defects revealed by the ^{18}O labelling. The origin of these defects is studied. Recent results (not presented) obtained by scanning tunnel microscopy suggest that these defects are related to the presence of small c-axis oriented inclusions in a-axis oriented matrix at the border of the sample.
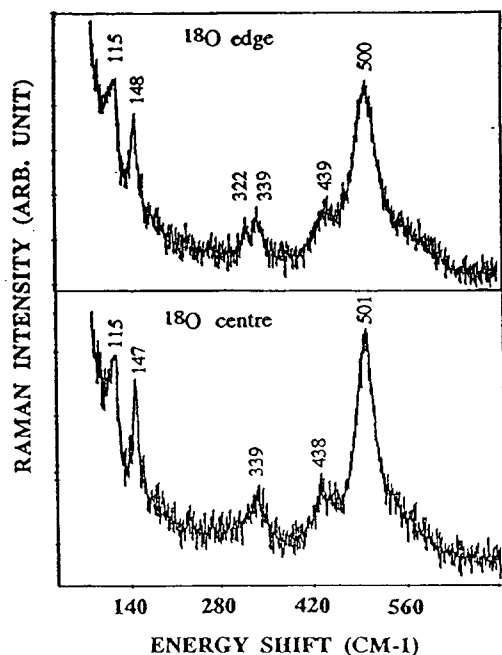

Fig.4. Raman spectra recorded on YBaCuO sample deposited on SrTiO$_3$ substrate and annealed in ^{18}O$_2$ atmosphere at 400°C. See texte for details; (a) recorded in the center of the sample, this spectrum is identical to as-prepared sample; (b) recorded at the edge of the sample.

4. Concluding remarks

On the basis of the thermodynamics and kinetics considerations, we performed an annealing treatement leading to the selective ^{18}O labelling of YBaCuO thin films. The ^{18}O content measured by NRA and the Raman spectroscopy confirm the selective ^{18}O labelling (until 90%) of the oxygen present in the CuO chain-planes, which is associated with the presence of good quality material. At the border of the sample, the presence of defective CuO$_2$ planes have been revealed combining the ^{18}O labelling and Raman Spectroscopy. Further experiments are carried out in order to study the disorder in the oxygen sublattice, in particular in the ^{18}O labelled CuO chain-planes, using the selective nuclear reaction resonances: $^{16}O(\alpha,\alpha)^{16}O$ and $^{18}O(p,\alpha)^{15}N$. The results will be published in a next paper.

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