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Oxygen doping tuning in superconducting oxides by thermal annealing and hard X-ray irradiation

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ABSTRACT

$Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconducting whiskers, owing to their microscopic size, are good candidates for the fabrication of miniaturized devices for production/sensing of THz-radiation based on their Intrinsic Josephson Junctions (IJJ) properties. With this respect, several studies demonstrated the possibility of controlling whisker IJJ parameters by modifying the oxygen content. In this paper we show that both thermal annealing and hard X-ray irradiation are effective ways to tune the oxygen doping. In particular, we monitored the effect of an annealing process at 363 K and of irradiation by 17 keV micro- and nano-beams on the structural and superconducting properties of selected Bi-2212 whiskers. Moreover we modeled by a finite element simulation the temperature field induced by the X-ray beam to try to clarify the origin of the measured changes.

1. Introduction

Since a few years ago whisker-like crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) [1,2] attracted significant attention because of their very good crystalline quality, peculiar dimensions with micrometric cross sections, leading to high aspect ratios, and outstanding superconducting properties [3,4].

The presence of a layered structure along the crystal c-axis, consisting of alternating superconducting and insulating planes, induces the intrinsic Josephson effect in this compound [5] and several studies have been published describing the possibility of producing or sensing coherent THz radiation using these materials [6–8]. Furthermore, some authors have reported on the possibility of controlling whisker intrinsic Josephson junction (IJJ) parameters (*e.g.* the critical current density and the junction resistance) by modifying the oxygen content, which is well known to be strongly related to the carrier density [9,10].

Previous investigations by our group showed that the Bi-2212 whiskers can undergo an aging process when exposed to air at 273 K or to a helium atmosphere at room temperature for long periods (100 days) [11,12], or when annealed at moderate temperature for few hours [13]. These processes are associated with oxygen depletion mechanisms, which lead to a modification of the *c*-axis length, and can be exploited to modulate the IJJ characteristics. Therefore a combined *in situ* structural and electrical characterization can help to better understand the ageing processes which can be crucial for the technological applications of these materials.

Also particle and photon irradiation has proven to be able to modify the structural and functional properties of these materials. The effect of heavy ion irradiation on Bi-2212 has been extensively investigated, showing that the critical temperature (T_c) starts to decrease when the fluences are higher than $\sim 1–2 \times 10^{11}$ ions cm^{-2} [14]. Also electron irradiation can induce polycrystallinity and amorphization in the whiskers at fluences of $\sim 10^{22}$ e^- cm^{-2} [15], whereas protons and α particles can knock O atoms out of the material at fluences of $\sim 10^{16}$ particles cm^{-2}, affecting both T_c and the normal state resistivity [16].

Concerning photons, Ishibashi et al. [17] reported that γ-rays of about 1.3 MeV are able to induce the desorption of extra oxygen atoms from the BiO layers of Bi-2212 and to reduce the size of the crystallites. Also other studies highlighted that γ-rays with similar energy can modify the oxygen concentration and the carrier

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distribution in different high temperature superconductor compounds [18,19]. In general, less energetic photons were considered unable to produce significant effects, but in the last decade great improvements have been performed in the focusing of X-ray beams at synchrotron sources [20,21], opening new possibilities for the study and manipulation of oxide superconductors [22,23]. Recently we showed that it is possible to locally tune the oxygen doping content by irradiating the material with an intense 17 keV X-ray nano-beam [24] and this process can be exploited to fabricate electrical devices, paving the way to a novel X-ray nano-patterning method that in principle can be extended to all oxide materials [25].

In this paper we present a comparative study of the effect of an annealing process at 363 K and of hard X-rays irradiation by X-ray micro- and nano-beams on selected Bi-2212 whiskers. Since such treatments are expected to induce variations in the oxygen content in the micro-crystals, we monitored the *c*-axis parameter evolution by X-ray diffraction and we investigated the changes in the electrical properties.

2. Experimental

2.1. Samples synthesis

The Bi-2212 whiskers were grown starting from high purity commercial powders of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO (Aldrich 99.9999%) finely mixed in Bi:Sr:Ca:Cu stoichiometric ratios of 1.5:1:1:2. The mixture was melted at 1050 °C and glassy plates were produced by quenching the melt between copper plates at room temperature. The growth of the crystals took place on the plates during a five day annealing at about 850 °C in a controlled O_2 flow. Such conditions were selected in order to obtain whiskers with doping features corresponding to the nearly optimally doped or slightly overdoped state to minimize the possible presence of defects due to oxygen vacant sites [26]. The Bi-2212 sample measured in the X-ray microprobe configuration has a size of $700 \times 5.17 \times 0.70\ \mu m^3$, while the whisker analyzed using the X-ray nanoprobe has a size of $600 \times 13.6 \times 1.59\ \mu m^3$.

2.2. Electrical measurements

The sample preparation procedure consists of the selection under an optical microscope (100× magnification) of a smooth and linear crystal. Then a chip which allows both electrical and structural measurements on the same crystal was obtained by mounting the whisker onto a sapphire substrate where four point contacts were obtained by Ag physical vapour deposition [27]. Such contacts were subsequently covered with Au to avoid oxidation and subjected to thermal diffusion at 450 °C for 5 min in pure oxygen atmosphere. The SEM micrograph in Fig. 1d shows a typical whisker (the *c*-axis is perpendicular to the sapphire substrate) with its four contacts perpendicular to the crystal. Each sample was electrically characterized along its *ab* crystallographic plane by the standard four-probe method with a 1 μA current.

2.3. X-ray micro- and nano-beam set-ups

The former ESRF ID22 beamline was installed on a high-β straight section of the ring equipped with two different undulators. After the front-end, the beam passed through the optics hutch (see Fig. 1a), where a set of selectable high-power filters and slits with adjustable horizontal and vertical apertures optimized the intensity and the shape of the beam. A flat horizontally deflecting Si mirror also allowed thermal load reduction and higher harmonic rejection, then the beam entered in a Kohzu fixed-exit Si(111) double crystal monochromator.

The microprobe set-up (experimental hutch EH1, see Fig. 1b) was based on Kirkpatrick-Baez (KB) mirrors that allowed us to reach a spatial resolution of 1.7 μm (vertical) × 5.3 μm (horizontal) with a photon flux $I_0 = 10^9$ photon s^{-1} at 17 keV. After passing in the micro-beam experimental hutch EH1, the beam entered in the nano-imaging experimental hutch EH2 (see Fig. 1c). The nano-focusing optics, located at 64 m from the undulator source, consisted of two graded multilayer coated surfaces mounted in crossed Kirkpatrick-Baez configuration. This design provided a reflectivity of 73% at 17 keV and a beam size of 117 (vertical) × 116 (horizontal) nm^2, with a photon flux $I_0 = 1.9 \times 10^{11}$ photon s^{-1} during our experiment. In both EH1 and EH2 experimental hutches different detectors were present: a mini-ionization chamber to monitor the intensity of the incoming beam, a Silicon Drift Detector (SDD) to acquire the XRF signals and a FreLoN CCD detector to collect micro-/nano-XRD patterns in transmission mode [28].

The chip holding the Bi-2212 whisker was alternately mounted in the ID22 hutch and in an off-line cryostat to allow complementary micro-/nano-XRD and electrical characterization on the same micro-crystal.

3. Results and discussion

3.1. Thermal annealing and micro-beam irradiation effects

The combination of resistivity *versus* temperature (R *vs* T) and micro-XRD measurements allowed firstly to clarify the effects of the exposure to hard-X ray micro-beam and the subsequent thermal annealing process on the oxygen content in an individual Bi-2212 whisker. Indeed, the evaluation of both electrical (*e.g.* the critical temperature T_c for the superconducting transition and the normal state resistivity ρ) [9,10,29] and structural parameters, primarily the *c*-axis length [10], allows to obtain detailed information on the oxygen content, which is nearly proportional to the carrier density in the superconducting cuprate. In particular, for the *c*-axis and ρ values a monotonous increase is expected upon oxygen depletion. Conversely, the T_c value increases while moving from overdoped to optimally-doped Bi-2212, reaches its maximum in correspondence of the optimal doping condition ($\sim 2.2 \times 10^{21}$ carriers/cm^3) and then decreases entering the underdoped regime [9,10,29]. With this respect, we employed the X-ray micro-probe of the former ESRF ID22 beamline to compare the impact of X-ray exposure to the effect of the thermal annealing on the local structural features of the Bi-2212 whiskers.

As discussed in a previous study [13] and hereinafter summarized, the significant *c*-axis elongation observed after a 6 h annealing at 363 K correlated with the modifications detected in the electrical properties, globally evidencing a decrease in the oxygen content from almost optimally doped to underdoped, for the as-grown and annealed whisker, respectively [13]. However, more detailed insights on the mechanism underlying the oxygen depletion process can be obtained considering also the oxygen doping modification induced by the micro-beam, whose properties are reported in Section 2.

It is worth noting that, in order to allow a quantitative comparison between the different X-ray irradiation conditions that we tested, including micro-beam and nano-beam (*vide infra*, Section 3.2) exposures, the dose D can be calculated according to Eq. (1):

$$D = \frac{I_0 \Delta t E_{abs}}{m_{I_0}} = \frac{I_0 \Delta t E_0 \left(1 - e^{-\frac{t}{\lambda_a}}\right)}{V_{I_0} \rho_m} \quad (1)$$

where Δt is the total time of irradiation, E_{abs} the absorbed photon energy, m_{I0} the irradiated mass of Bi-2212, V_{I0} the irradiated volume, ρ_m the mass density, x the material thickness and λ_α

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