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(Article begins on next page)



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# Control of the oxygen doping in Bi-2212 whiskers by means of their synthesis process

M M Rahman Khan<sup>1,2</sup>, S Cagliero<sup>1,2</sup>, A Agostino<sup>1</sup>, M Beagum<sup>1,2</sup>, C Plapcianu<sup>1,2</sup> and M Truccato<sup>2</sup>

<sup>1</sup> NIS-Centre of Excellence, Department of General and Organic Chemistry, University of Torino, Corso Massimo D'Azeglio 48, I-10125, Torino, Italy

<sup>2</sup> NIS-Centre of Excellence, Department of Experimental physics, University of Torino, Via P Giuria 1, I-10125, Torino, Italy

E-mail: truccato@to.infn.it

## Abstract

Direct evidences of oxygen doping control in single phase  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212) whisker are reported, along with the changes in their structural properties obtained by varying the growth temperature of the synthesis process in the range from 843°C to 872°C. The as grown whiskers were investigated by means of X-Rays Powder Diffraction (XRPD), electrical transport measurements, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). The XRPD measurements showed that the value of  $c$ -axis lattice parameter increases from 30.556Å to 30.640Å when increasing the growth temperature, which indicates different oxygen doping levels spanning from the slightly overdoped to the nearly optimally doped regimes. Such results are also confirmed by the electrical characterizations, which revealed a typical relationship among resistivity ( $\rho_{ab}$ ), superconducting critical temperature ( $T_c$ ), and  $c$ -axis value. The growth of CuO crystals has also been identified during this study, with a maximum yield in the range 860°C-864°C, where also a slope change in the  $c$ -axis behaviour has been found, implying a possible correlation between the two phenomena. Therefore, by changing the synthesis growth temperature, one can provide an effective way for tuning the whisker electrical transport properties.

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**Keywords:** Bi-2212, whisker, growth temperature, doping, XRD,  $c$ -axis, resistivity

## 1. Introduction

Suitable materials for the fabrication of TeraHertz (THz) radiation sources represent a challenging research subject, due to various application domains such as radiation technologies, physical, biological, medical and applied sciences [1-3]. Materials able to fulfill the demand for fabrication of THz radiation sources are presently intensively studied. Several works can be found demonstrating the possibility to produce or sense coherent THz radiation from layered high-temperature superconductors (HTSC) due to their intrinsic Josephson junctions (IJJs) properties [1, 4, 5]. For instance, the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Bi-2212) phase of the BSCCO system exhibits such features and has been widely studied in previous papers [6-8]. In this framework, Bi-2212 crystals in the form of whiskers represent good candidates for device fabrication because of their high crystalline quality and microscopic sizes [9]. Many mechanisms have already been proposed for their growth so far, as summarized in the review by Badica *et al.* [10]. Among the already performed experiments, many studies investigated the influence of the synthesis temperature, especially from the point of view of its relationship with the precursor cationic composition [11-15]. However, all of them were much more focused on the amount and length of the produced material than on its structural and electronic properties, so that a clear understanding of their correlation with the synthesis temperature is presently lacking [10].

On the other hand, the ability to control the IJJs parameters of Bi-2212 whiskers is very important in order to fabricate reliable devices. So far, all of the achievements in this field have been obtained by means of post-annealing treatments to be applied after the growth stage. Typical treatments consisted of post-annealing temperatures around 400°C [8, 16], even if it has been shown that similar effects can also be obtained at much lower temperatures [17, 18, 19]. Such processes are able to induce remarkable modifications in the oxygen doping level that can be detected by means of the *c*-axis lattice parameter [16, 17, 20, 21], but can also give rise to a certain degree of unhomogeneity in the whiskers [18, 19].

Therefore, an investigation of the effects of the synthesis temperature used during the growth stage on the electronic properties of single phase Bi-2212 whiskers is needed, both for the lack of information in the field and in order to achieve the direct control of the electronic properties avoiding further post-annealing treatments. The present study represents a trial to tackle this problem in the case of fixed atmosphere composition and gas flow rate, characterizing the structural and electronic properties corresponding to the different synthesis temperatures by means of XRD and electrical transport techniques.

## 2. Experimental procedure

The samples studied in this work were synthesized according to the “glassy plate” method [22, 23] starting from individual component oxides. Highly pure reagent powders of  $\text{Bi}_2\text{O}_3$  (99.99%),  $\text{SrCO}_3$  (99.9999%),  $\text{CaCO}_3$  (99.99999%) and  $\text{CuO}$  (99.999999%), (Sigma-Aldrich, Germany) were thoroughly mixed with nominal composition  $\text{Bi}_{1.5}\text{Sr}_1\text{Ca}_1\text{Cu}_2$  and melted at  $1200^\circ\text{C}$  in a box furnace to produce glassy plates by means of splat cooling process. It is well known that during this part of the process Al impurities are incorporated in the glassy precursors from the  $\text{Al}_2\text{O}_3$  crucible, and can work as seeds for the whisker growth [24]. The glassy plates were then heated with a ramp rate of  $5^\circ\text{C}/\text{min}$  up to different growth temperatures ranging from  $843^\circ\text{C}$ - $875^\circ\text{C}$  and kept in these conditions for 7200 minutes with a controlled oxygen flow (0.2 l/min), as reported in table 1. Then the samples underwent a cooling ramp with a constant rate ( $5^\circ\text{C}/\text{min}$ ), down to room temperature. Since the heating and cooling rates were kept constant for all the syntheses, this resulted into a difference on the process total time of 11.6 minutes between the lowest and highest growth temperature syntheses. This corresponds to a maximum relative time difference of 1.5‰ between the batches, which is expected to have negligible influence on the whisker structural and electrical properties and for this reason is usually not reported by other authors [11-15].

The general morphology and the length, width, and thickness of the synthesized whiskers were observed by SEM (LEICA STEREOSCAN 420) and AFM (XE-100 Park System). The local elemental composition of the crystals was studied by EDS to investigate the cationic stoichiometry both for Bi-2212 whiskers and for other structures grown on the glassy plates.

Two different sets of whiskers were chosen: one for the XRPD and another one for the electrical measurements. Concerning the XRPD measurements, whiskers with smooth and regular surfaces were selected at the optical microscope (LEICA 150X) from each freshly synthesized batch and were positioned on amorphous quartz supports for diffractometry. The crystals were placed with their largest surfaces parallel to the plane of the substrate, which normally results in a *c*-axis orientation perpendicular to it. It is very likely that whiskers with smaller cross section areas show lower defectiveness (for example, dislocations, twinning, etc.) [25, 26]; for this reason, following the same procedure already described in a previous paper by our group [18], we selected the whiskers by trying to obtain good reflections, but also by compromising between a high XRD signal to noise ratio and low sample dimensions. Consequently, we prepared samples according to the characteristics listed in table 1. XRPD data were obtained from X’Pert Analytical instrument equipped with Cu target and X’Celerator ultrafast line detector; the measurements were performed in theta-theta geometry with  $\text{CuK}\alpha$  radiation and an angular step size  $0.02^\circ$ .

In order to obtain the whiskers  $c$ -axis values, we fitted each peak of the patterns with the Fytk (GPL) program [27]. The fits were obtained with one Gaussian function per each component of the double peak due to the  $\text{CuK}_{\alpha 1}$  and  $\text{CuK}_{\alpha 2}$  radiations. Then we calculated the  $c$ -axis of the crystal by means of the least-squares refinement program Unitcell [28], using only the reflections due to the  $\text{CuK}_{\alpha 1}$  wavelength because of their higher intensity. All of the Bragg peaks obtained in the  $2\theta$  range  $5^\circ \div 70^\circ$  were investigated to analyze the structural properties of the Bi-2212 phase whiskers.

**Table1.** Resume of the characteristics of the samples from different synthesis batches. The synthesis identifiers, growth temperatures, number of whiskers used in each XRPD experiment and their approximate mean length (mm),  $c$ -axis values,  $T_c$ 's, amount and shape of CuO structures are listed. No  $T_c$  value is reported for  $\alpha$  batch, since no single phase sample was found. For the synthesis batch  $\eta$ , no whiskers were obtained due to the glassy plate melting. Number and length of the vertical lines indicated in the CuO structures column represent number and length of the grown CuO structures (see text).

Synthesis identifier	Growth temperature ( $^\circ\text{C}$ )	No. of whiskers for XRPD measurement	Approximate mean length (mm)	$c$ -axis value ( $\text{\AA}$ )	$T_c$ (K)	CuO structures
$\alpha$	$843 \pm 1$	3	2	$30.556 \pm 0.002$	-	■
$\beta$	$855 \pm 1$	4	1	$30.575 \pm 0.002$	$77.4 \pm 0.1$	■■
$\gamma$	$860 \pm 1$	4	1	$30.582 \pm 0.002$	$77.7 \pm 0.1$	■■■■
$\delta$	$864 \pm 1$	3	2	$30.584 \pm 0.002$	$78.6 \pm 0.1$	■■■■
$\epsilon$	$869 \pm 1$	4	1	$30.620 \pm 0.002$	$79.0 \pm 0.1$	■■
$\zeta$	$872 \pm 1$	3	2	$30.640 \pm 0.002$	$79.8 \pm 0.1$	■■
$\eta$	$875 \pm 1$	-	-	-	-	-

In order to prepare samples for electrical characterization, we selected one as-grown and very regular BSCCO whisker from each of the fresh synthesis batches. We fabricated electrical contacts by thermally evaporating on the whiskers  $2.5 \mu\text{m}$  thick silver films covered by  $35 \text{ nm}$  thick gold layers and by diffusing them at  $450^\circ\text{C}$  for 5 minutes in pure oxygen atmosphere [29]. This way, micrometric chips were produced with metal contacts perpendicular to the whisker.

Then resistivity vs. temperature data were acquired by means of the standard four probe technique. All of the resistivity measurements were obtained by cycling the micro-chips between liquid nitrogen temperature and room temperature at the average rate of  $0.2 \text{ K/min}$  and by feeding the crystals with current pulses in the  $1\text{-}5\mu\text{A}$  range. In order to be able to make exact correlations with the Bi-2212 phase only and therefore to avoid any interplay with the possible presence of the Bi-2223 phase, only

samples showing pure Bi-2212 behavior were retained for this study. The  $T_c$  was evaluated for each whisker as the inflection point of the resistivity curves.

### **3. Results and Discussions**

#### *3.1 SEM and EDS analysis:*

SEM and EDS analyses were performed on all of the six batches presented in table 1, obtaining elemental and morphological characterizations. Figure 1 shows three SEM micrographs captured for the  $\beta$  (panel a),  $\delta$  (panel b) and  $\epsilon$  (panel c) synthesis batches. In panel (a) a Bi-2212 whisker is clearly visible, and looks like those selected for the electrical characterizations. Similar crystals were found in all of the other batches. Compositional analysis by EDS of such whiskers always revealed atomic ratios around Bi:Sr:Ca:Cu=32:20:19:29, while the composition of Al is below the instrument detection limit. These stoichiometries are very similar to those reported for Bi-2212 whiskers by several authors in previous works on whiskers, taking into account the Sr on Ca substitution typical of such crystals [24, 30].

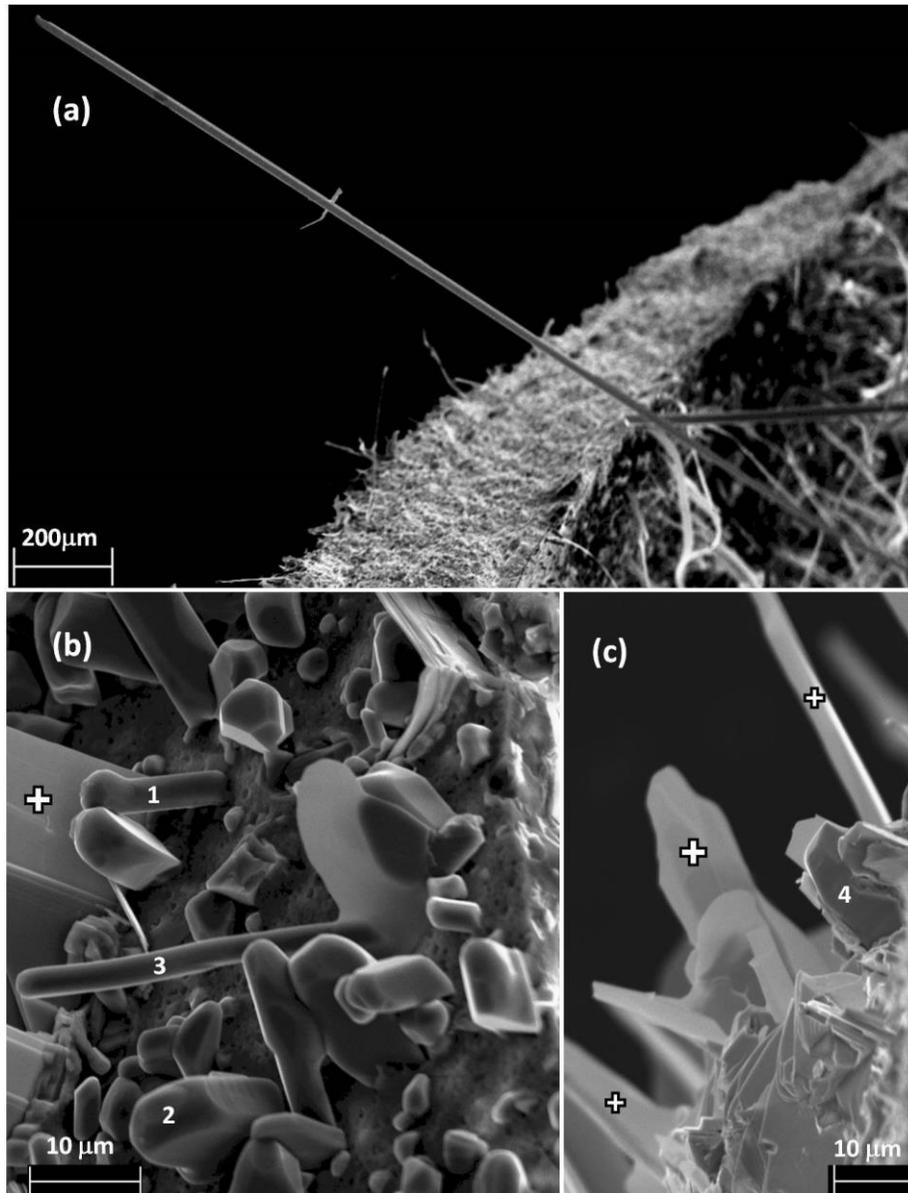


Figure 1: SEM images of Bi-2212 and CuO crystals obtained from different syntheses. Panel (a) corresponds to  $\beta$  batch and shows a typical Bi-2212 whisker; panel (b) represents  $\delta$  batch: CuO crystals are labelled by numbers 1, 2 and 3, while a Bi-2212 whisker is marked with a white cross; panel (c) was obtained on  $\varepsilon$  batch and reports a CuO crystal (number 4) surrounded by Bi-2212 whiskers (white crosses). Numbers from 1 to 4 and white crosses indicate the points where EDS analyses were performed.

In all of the analyzed batches we also found other structures grown on the annealed glassy plates. Such structures were composed of Cu for 98% (EDS analyses are reported in table 2), this composition was already identified by Matsubara *et al* [30] and defined as CuO phase. An example is represented by the cuboids marked with number 2 in panel (b) and number 4 in panel (c) of figure 1. Structures marked with

numbers 1 and 3 in the same panel are more elongated crystals (with aspect ratio about 1:10) of the same material. It is noteworthy that the number of cuboid structures varies with the growth temperature, being maximum in the range 860°C-864°C ( $\gamma$  -  $\delta$  batches), which is also the only temperature range where elongated CuO structures can be observed (see table 1). This can also be appreciated by the comparison between panel (b) and (c) of figure 1, where, in the latter, only one massive CuO crystal is surrounded by Bi-2212 whiskers (marked by white crosses).

**Table 2.** Results of EDS analyses of the CuO structures of panel (b) and (c) of figure 1. ND means that element is below the detection limit.

Position	Atomic ratio (at %)					Phase
	Bi	Sr	Ca	Cu	Al	
1	1	1	ND	98	ND	CuO
2	2	1	ND	97	ND	CuO
3	8	6	5	81	ND	CuO
4	1	1	ND	98	ND	CuO

Similar CuO growths have been already observed by other researchers. Yamada *et al* [31] observed the presence of CuO whiskers during synthesis processes starting from different doped precursors, but with growth temperatures in the range 850°C-890°C, depending on the used impurities. In our case, we did not use doped precursors (except for the Al impurities incorporated from the crucible), but similar values of temperature were adopted. Badica and Togano [24] also reported the growth of ribbon-like CuO structures by applying high magnetic fields in the synthesis process, while they observed only 2D crystals in syntheses without magnetic field, and in regions of the glassy plates where a higher amount of Al impurities was present. We think that our results, showing the production of CuO ribbon-like structures for syntheses without magnetic field, could be due to the influence of higher growth temperatures applied in the present work, with respect to the lower range of growth temperatures (840°C-855°C) investigated in [24].

### 3.2: XRPD and electrical characterization results

Figure 2 shows, for instance, the XRPD measurement of whiskers obtained from  $\delta$  synthesis batch, where only 00l reflections belonging to the Bi-2212 phases are noticeable, excluding at a first approximation, within the limit of X-ray diffraction analysis, the presence of other phases. Anyway, it is well known that the occurrence of other phases of the BSCCO system could not be appreciated by XRPD measurement, due to the small volume contribution [23]. According to the pattern shown in figure 2, it is also clear that the whiskers were all aligned with their  $c$ -axis perpendicular to the substrate. All of the other samples gave similar diffraction patterns.

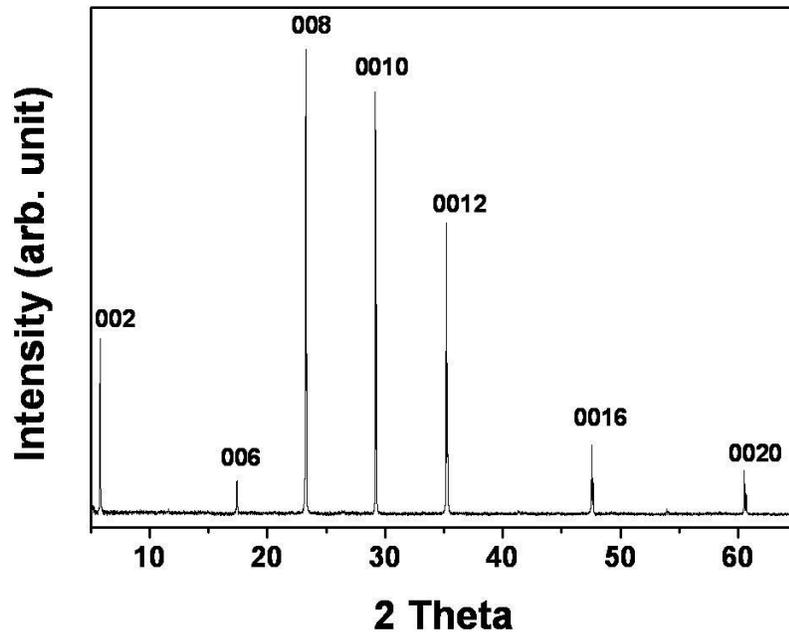


Figure 2: XRPD pattern for the sample synthesized at 864°C growth temperature ( $\delta$  batch) obtained in as-grown conditions. Background signal has been subtracted.

The  $c$ -axis values evaluated from the XRPD patterns are listed in table 1 and plotted as a function of the temperature in figure 3. It is found that the  $c$ -axis lattice constant of the whiskers increases when the growth temperature of the synthesis process increases; such  $c$ -axis behavior can be associated with the oxygen content in the crystals, as mentioned in several studies [16, 17, 20, 21].

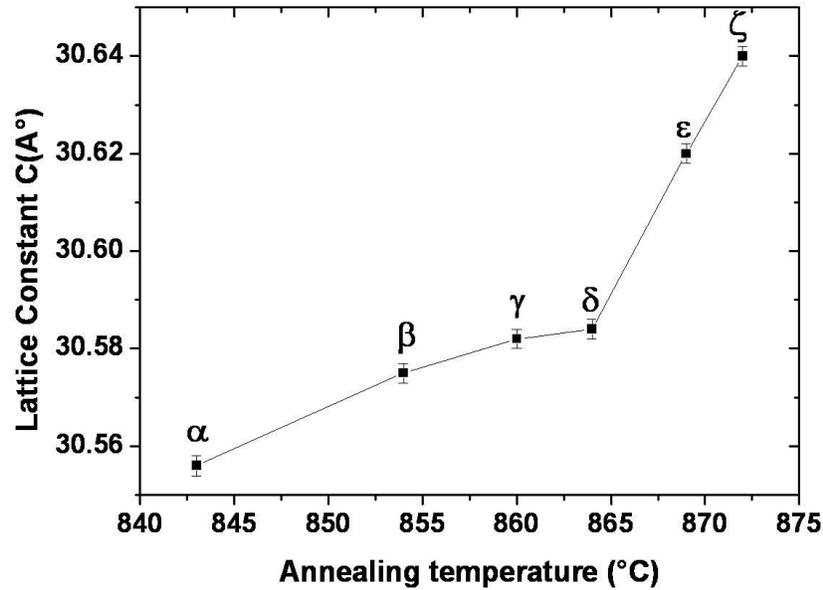


Figure 3:  $c$ -axis lattice constant for Bi-2212 whiskers versus the synthesis growth temperature (Greek letters refer to the synthesis batches reported in table 1).

It is possible to notice that the  $c$ -axis lattice parameter monotonically increases from the lowest temperature (843°C) to the highest one (872°C) used for the different synthesis batches, spanning the 30.556Å ÷ 30.640Å  $c$ -axis range. As already shown in several studies [16, 17, 20, 21], this trend can be explained by a lower oxygen incorporation in the crystals when increasing the growth temperature. It was not possible to obtain data for the temperature 875°C, as the glassy plate was melted. The  $T_c$  values for all of the syntheses are also listed in table 1 showing a defined increasing behavior, which is correlated to the  $c$ -axis values dependence on the growth temperatures. Such a direct correlation between the  $T_c$  values and the  $c$ -axis parameters is also presented in figure 4 which supports the conclusion of lower O<sub>2</sub> content incorporation when increasing the growth temperature.

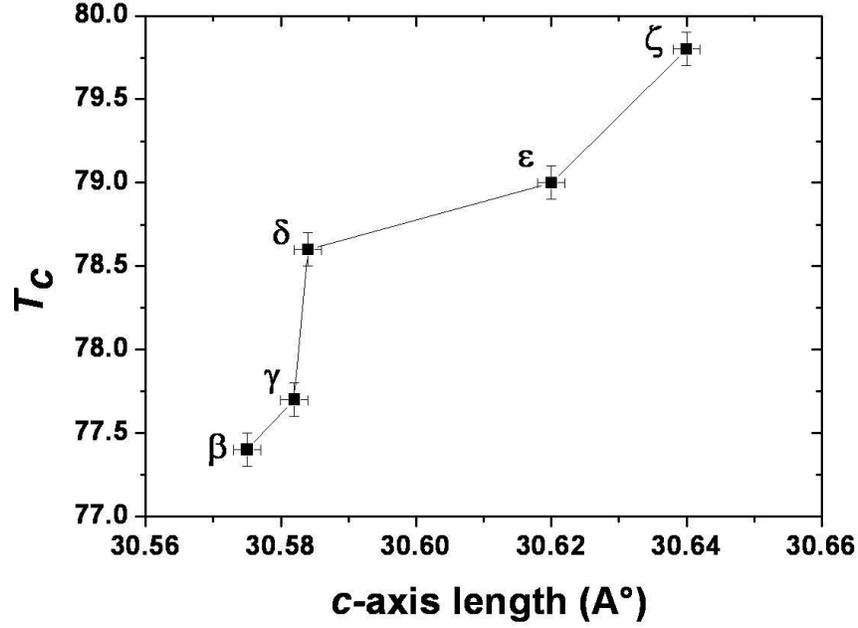


Figure 4: Plot of the  $T_c$  values vs the  $c$ -axis lattice parameters of the whiskers collected from the different synthesis batches. Greek letters are the synthesis identifier as reported in table 1. Error bars for both the  $T_c$  and  $c$ -axis values are reported.

By comparing these values with those reported by Inomata *et al* [16], it can be deduced that the  $c$ -axis values of the Bi-2212 whiskers grown in the 843°C-864°C range correspond to the overdoped regime, the ones obtained on whiskers from 869°C and 872°C batches approach the optimally doped regime, which is also confirmed by another work [17].

However, it can be noted that our measurements are slightly shifted towards different  $T_c$  values. This could be due to the different methods used for the whisker synthesis (no Te is included among our precursors) and to the fact that these authors used post-annealing treatments to change the electronic properties. Probably more relevant, we have also to stress that the previous results by Inomata *et al* [16] concern the so-called  $T_{c,end}$ , i.e. the superconducting transition temperature corresponding to the Bi-2212 phase in a sample that also contains some amount of the Bi-2223 phase. We have already shown in a previous study [32] that the interplay between these two phases in a single sample is characterized by a strong influence of the Bi-2223 phase on the  $T_c$  of the Bi-2212 phase, because of the possible modification of the oxygen ion content in the Bi-2212 phase and therefore leading to quite unusual  $T_c$  values. Therefore, since in the  $\alpha$  synthesis batch it was not possible to find whiskers with a single

superconducting transition because of the intergrowths with Bi-2223 phase, we did not report any corresponding  $T_c$  value both in table 1 and figure 4 for consistency reasons.

It can also be noticed that the  $T_c$  value corresponding to 78.6K ( $\delta$  batch) seems to present a slight deviation from the general trend. This discontinuity is not a random one, as it corresponds to the change in the slope of the  $c$ -axis vs growth temperature curve observed in figure 3 for the  $\gamma$ ,  $\delta$  and  $\epsilon$  batches. Such a scattering in  $T_c$  data for almost identical  $c$ -axis values is less than the one shown in the range 30.58Å to 30.60 Å by other researchers [8].

The growth temperature does not only affect the  $T_c$  values but also the resistivity behavior of the whiskers. This is presented in figure 5, showing the  $\rho_{ab}$  vs T measurements of three Bi-2212 whisker selected from  $\beta$  (855°C),  $\delta$  (864°C) and  $\epsilon$  (869°C) synthesis batches. Their  $c$ -axis lengths are also reported in the same figure.

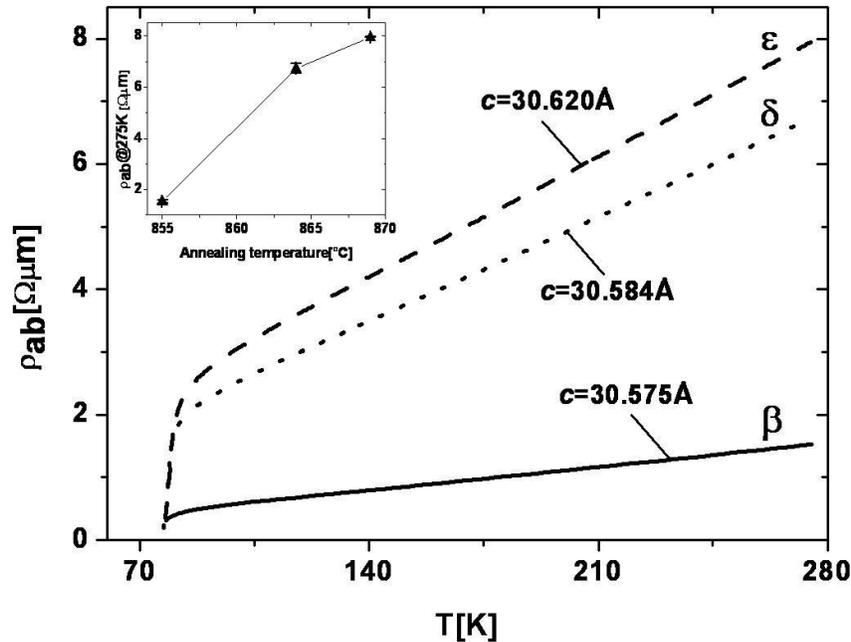


Figure 5: Resume of the temperature dependence of in-plane resistivity  $\rho_{ab}$  of Bi-2212 whisker samples selected from synthesis batches  $\beta$ ,  $\delta$  and  $\epsilon$ :  $\beta$  corresponds to temperature 855°C (solid curve),  $\delta$  to 864°C (dotted line) and  $\epsilon$  to 869°C (dashed line). For each sample, the corresponding  $c$ -axis values of whiskers selected from the same batch are also reported. The inset shows the resistivity value at 275K vs growth temperature of these 3 whiskers. Solid bars are the corresponding error for resistivity at 275K.

It is apparent that the  $\rho_{ab}$  curves are shifted towards higher values while increasing the growth temperature, as highlighted also by the inset, where the growth temperature dependence of  $\rho_{ab}$  at 275K for

the three samples is shown. Also the average slope ( $dp_{ab}/dT$ ) of these three curves changes with the growth temperature, which is a clear indication of different doping states resulting from the growth process for the whiskers [21]. Therefore, all of these observations confirm the conclusions drawn by the *c*-axis analysis that less doped whiskers can be obtained by means of higher growth temperatures.

Finally, it is useful to stress that the temperature region where a slope change in the *c*-axis vs. growth temperature curve takes place (i.e. between 860°C and 864°C) corresponds to the one where a higher amount of CuO structures is present. This could be related to the growth process for the Bi-2212 whiskers. However, we are not able to give a good explanation of such correlation and this makes such an interesting feature worthy of further investigation.

#### 4. Conclusions

Bi-2212 whiskers have been produced by means of different growth temperatures for the synthesis process. These crystals were investigated by XRPD, electrical transport measurements and SEM/EDS analysis. The data obtained by XRPD measurements on as-grown crystals show that the *c*-axis lattice parameter increases with increasing the growth temperature, which corresponds to an oxygen content modification from the slightly overdoped to the nearly optimally doped regime. This range of oxygen doping is also confirmed by the electrical characterizations, showing the typical relationship between  $\rho_{ab}$ ,  $T_c$  and the *c*-axis lattice constant. In the present experiment we have also observed the growth of CuO structures, whose amount and shape depend on the applied growth temperature, and shows some correlation with the temperature dependence of the *c*-axis values. This could imply a possible role of CuO in the Bi-2212 whisker growth.

All of the data represent direct evidences that control of the oxygen doping properties of Bi-2212 whiskers is possible by changing the growth temperature of the synthesis process. Therefore, a new method can be envisaged for tuning the properties of possible future THz devices based on Bi-2212 whiskers, which could also result in a lower degree of unhomogeneity compared to the methods based on post-annealing treatments.

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