

Evidence of ion diffusion at room temperature in microcrystals of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ superconductor

M. Truccato^{a)}

"NIS" Centre of Excellence, Dipartimento Fisica Sperimentale, and INFN UdR Torino Università, Via Pietro Giuria 1, I-10125, Torino, Italy

C. Lamberti and C. Prestipino

"NIS" Centre of Excellence, Dipartimento Chimica I.F.M., and INFN UdR Torino Università, Via Pietro Giuria 7, I-10125, Torino, Italy

A. Agostino

"NIS" Centre of Excellence, Dipartimento Chimica and Generale ed Organica Applicata, INFN UdR Torino Università, C.so Massimo D'Azeglio 48, I-10125, Torino, Italy

(Received 25 January 2005; accepted 28 April 2005; published online 20 May 2005)

We have studied Bi-2212 microcrystals aged at ambient conditions for 40 days. Combined x-ray absorption near edge structure and x-ray fluorescence measurements with micrometer space resolution show both an increase of Cu^+ with respect to Cu^{2+} and an enrichment in Cu vs Bi and Sr cation content near the sample edges in the b -axis direction. A parallel study on an electrically contacted sample has indirectly detected the O loss, observing both a resistivity increase and an increase in sample thickness near the edges. We conclude that the O outdiffusion along the b axis is accompanied by Cu cation migration in the same direction. © 2005 American Institute of Physics. [DOI: 10.1063/1.1938251]

Single crystals of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) high- T_c superconductor can be grown in samples whose length ($\geq 500 \mu\text{m}$) is much greater than both their width and their thickness (whiskers). These kinds of samples have recently attracted remarkable interest from the point of view of both basic and applied physics. In fact, they have proved to be suitable systems for the study of the excess conductivity above T_c (Ref. 1) and of the transport properties along the c axis² because of their high quality and small sizes. Moreover, they are also good candidates for the fabrication of microscopic electronic devices based on the intrinsic Josephson junction stack structure.³ Therefore, the check of the whisker homogeneity in terms of elemental and electronic structures has become an important issue. As far as bulk samples (i.e., with sizes greater than about $1000 \times 200 \times 10 \mu\text{m}^3$) are concerned, it is well known that the material properties can be tuned by annealing in proper atmospheres. This procedure usually involves temperatures above 400°C in order to ensure homogeneous oxygen diffusion throughout the sample on a few hours time scale,⁴ so that the O-diffusion length (λ) is much greater than the sample size (ℓ). On the other hand, it has already been shown that Bi-2212 whiskers can undergo a significant increase in the in-plane resistivity when aged at room temperature on a two-year time scale,⁵ most likely because of the oxygen loss induced by the favorable comparison between ℓ and λ .

Variations in the O nonstoichiometry of Bi-2212 whiskers must be accompanied by a change of the Cu oxidation state in order to guarantee the electrostatic neutrality of the crystal. If λ is smaller or comparable with ℓ , then a gradient in the O content, and therefore in the average Cu oxidation state, is expected. As Cu^+ and Cu^{2+} have very different chemical behaviors, a significant local modification around

Cu cations is expected when they undergo the oxidation state variation. Due to its chemical selectivity, the x-ray absorption near edge structure (XANES) is the most suitable spectroscopic technique able to investigate both the oxidation and the coordination state of a selected transition metal cation inside a matrix.⁶⁻⁹ As third generation synchrotron facilities provide microfocus beamlines, the determination of the local oxidation state of Cu inside aged Bi-2212 single crystals is possible at the micrometer scale. With this aim we have performed μ -XANES experiments at the ID22 beamline of the ESRF synchrotron.¹⁰ To verify whether the variation of the local Cu oxidation state, induced by O diffusion, is accompanied by a cation migration or not, x-ray fluorescence (XRF) has also been measured with the same spatial resolution of $1 \mu\text{m}$ (vertical) $\times 4 \mu\text{m}$ (horizontal).

In order to better appreciate the expected variation of the Cu oxidation state induced by O migration, samples were grown 40 days before the synchrotron measurements and aged at ambient conditions. The samples were prepared by the method of the oxygenation of melt quenched plates, resulting in crystals with typical dimensions of $500 \times 20 \times 1 \mu\text{m}$ along the a , b , and c axis, respectively. High-quality single crystals were selected at the optical microscope and either mounted on a glass capillary, for synchrotron measurements, or electrically contacted by Ag thermal evaporation and diffusion.⁵ The single-phase character of the samples was checked by a standard four-probe measurement of the electrical resistance R vs the temperature T . The typical $R(T)$ behavior is reported in the inset (a) of Fig. 1, which shows $T_c = 79.1 \text{ K}$. At the end of this experiment the sample was kept at room temperature for 12 h, then the $R(T)$ measurement was repeated, resulting in the scattered triangles reported in inset (b) of Fig. 1. To appreciate the small but significant shift of the $R(T)$ curve $\Delta R/R \approx 5 \times 10^{-3}$ only a limited T interval has been reported, but the same $\Delta R/R$ value holds over the whole measured T range. The observed

^{a)}Electronic mail: truccato@to.infn.it