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Oxygen in-diffusion processes in tetragonal $YBa_2Cu_3O_{7-x}$ oxide

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In situ resistance measurements have been used to investigate the oxygen in diffusion in tetragonal $YBa_2Cu_3O_{7-x}$ oxide. The oxygen content has been measured by nuclear reaction and by weighing; x-ray diffraction has been used to determine the crystalline structure. The polycrystalline bulk material with $x=0.65$ has been heated in oxygen to 200–370 °C. As a function of time the resistance curves continuously decrease and present two slopes: fast at the beginning and slow later. At first the material is tetragonal and nonsuperconducting. Complementary weight measurements indicate a significant increase only after a delay, and the oxygen uptake is associated with the slow variation of resistance. The initial slopes of the isothermal resistance versus time curves follow, in an Arrhenius plot, a straight line, suggesting a process with an activation energy of 0.40 ± 0.05 eV. The sharp decrease in resistivity can be attributed to the presence of a thin continuous conductive skin around the grains or, more likely, to a disorder-order transformation activated by the presence of oxygen and involving a large part of the material. A process having an activation energy of 0.9 ± 0.1 eV is responsible for the slow variation of the resistance. This is in agreement with published data obtained for oxygen in diffusion in similar conditions.

INTRODUCTION

The electrical properties of the high-T_c oxide superconductor $YBa_2Cu_3O_{7-x}$ are mostly affected by the oxygen content of the material.[1,2] The control of the processes at the basis of the oxygen uptake in the oxide is mandatory in order to have stable material with reproducible and reliable characteristics.

Oxygen in-diffusion studies[3-5] were performed in tetragonal samples obtained by high-temperature (900 °C) annealing in air. It has been shown that the tetragonal-orthorhombic transformation occurs in oxygen ambient in the 200–700 °C temperature range and that is kinetically controlled. By estimating the volume fraction of the superconducting phase from the magnetization versus field data it was supposed that the orthorhombic phase nucleates quickly along the grain boundaries, then propagates into the grain as a planar front governed by the much slower volume diffusion of oxygen. Planar diffusion has also been found by Tu, Yeh, Park, and Tsuei[6] who studied the oxygen in diffusion in orthorhombic $YBa_2Cu_3O_{6.6}$ oxide with *in situ* resistance measurements. According to these authors the oxygen transport can occur through two different mechanisms characterized by two different activation energies: 0.48 eV at $x=0.38$ due to the motion of oxygen and 1.1 eV at $x=0$ due to its diffusion. The latter activation energy is the sum of the energy necessary to create a defect plus the energy of motion. A similar detailed analysis of the tetragonal phase has not previously been performed; moreover, the results of such an analysis are particularly interesting since in the present superconductor compound production techniques the oxidation is initiated in the tetragonal phase.

The purpose of the present paper is to investigate the oxygen uptake in the tetragonal superconductor oxide by combining *in situ* resistance and thermogravimetric measurements. We will show that there are two important processes, one with a large resistance variation and none or little oxygen absorption and the second with planar diffusion in an oxide having an oxygen content of at least $x=0.2$.

EXPERIMENT

Samples having composition of $YBa_2Cu_3O_{6.9}$ were prepared from a mixture of stoichiometric proportions of Y_2O_3, $BaCO_3$, and CuO powders.[7] The material was polycrystalline in the form of platelets with a large distribution of grain size. Along the c axis most of the grains have thicknesses of 10–20 μm; the major dispersion occurs in the a, b directions with grains having sizes from tens to hundreds of μm. Voids are present in the material and the density is 75% of the bulk material. The presence of voids allows the material to be treated as single grains with respect to the in and out diffusion of oxygen.

In situ sheet resistance measurements were performed by using spring-loaded wires in contact with gold dots that are sputter deposited on a surface of the superconductor sample in the Van der Pauw configuration. The in-diffusion of oxygen was studied by inserting the sample into the cool furnace in argon ambient and heating up to 700 °C at 5 °C/min; after 50-min equilibration time, the sample was cooled down to the desired temperatures, 200 to 370 °C, still in Ar ambient. After a waiting period of about 30 min the oxygen gas was switched on. Less than 1 min elapsed between the switch of the gas and the initial decrease of the resistance.

In situ thermogravimetric measurements were performed following the same heat treatments previously described for resistance measurements. The apparatus is a Netzsch STA 409 system having a sensitivity of 10^{-4}. Before and after each heat treatment the samples were weighed at room temperature in a separate system and the results were found to be in agreement with those obtained during the *in situ* measurements.

The oxygen concentration was measured using the $^{16}O(d,p_1)^{17}O$ nuclear reaction.[8] Relative measurements were performed utilizing, as a reference, an as-prepared Y-Ba-Cu-O disk with a nominal oxygen concentration of 6.90 ± 0.02. Deuterons impinging at 880 keV lose about 60 keV/μm in the oxide; by combining the scattering cross section with the differential energy loss value the sampled depth was estimated at about 2–3 μm.

Low-temperature resistivity measurements were performed using an apparatus described previously.[9]

A Bragg-Brentano configuration and a Cu $K\alpha$ Ni-filtered x-ray source were used to identify the structure and to measure the lattice parameters. The lattice parameter was determined by a least-squares best-fit procedure[10] taking into account the diffraction intensities from single-crystal measurements.[11] More than 30 peaks were used for both the orthorhombic (35) and the tetragonal (30) phases, arriving at an estimated standard deviation of 10^{-3} Å.

RESULTS

Heat treatment at 700 °C in an argon atmosphere produced the tetragonal oxide with an oxygen content of $x=0.65$; moreover, *in situ* thermogravimetric measurements indicated that the cooling in Ar did not modify the oxygen content of the sample. In the 200–300 °C temperature range the change from argon to oxygen produced, as a function of time, a continuous decrease of the sheet resistance. The inset in Fig. 1 shows a curve obtained at 215 °C up to 1000 min. Time zero is defined as the moment of oxygen introduction. Two slopes are clearly present; the first one is evident in Fig. 1, where a set of experimental resistance curves obtained during various isothermal treatments is reported as a function of time up to 20 min. Since the material in the tetragonal form behaves as a semiconductor and the resistance decreases with increasing temperature, the curves were normalized at the resistance values measured just before the introduction of the oxygen gas. To establish a correlation between resistance and some other physical property, samples were quenched to room temperature when they reached a predetermined resistance value. It was assumed that the quenching did not modify the structure and composition, and the various measurements performed at room temperature revealed the sample configuration at elevated temperatures.

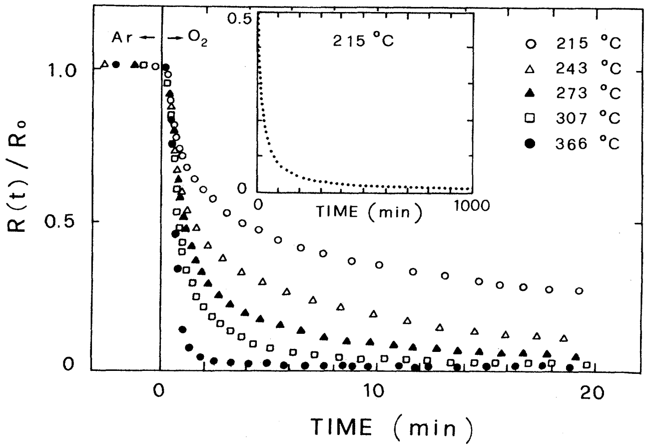

FIG. 1. Normalized sheet resistance measurements as a function of the annealing time. R_0 is the resistance value measured just before the introduction of the oxygen gas. The inset shows a full curve measured up to 1000 min at 215 °C.

Figure 2 shows the weight change during isothermal treatments at various temperatures obtained by *in situ* thermogravimetric measurements. Again the time zero was defined by the oxygen introduction. The weight increased after a certain delay, the duration of which decreased with increasing treatment temperature. At the

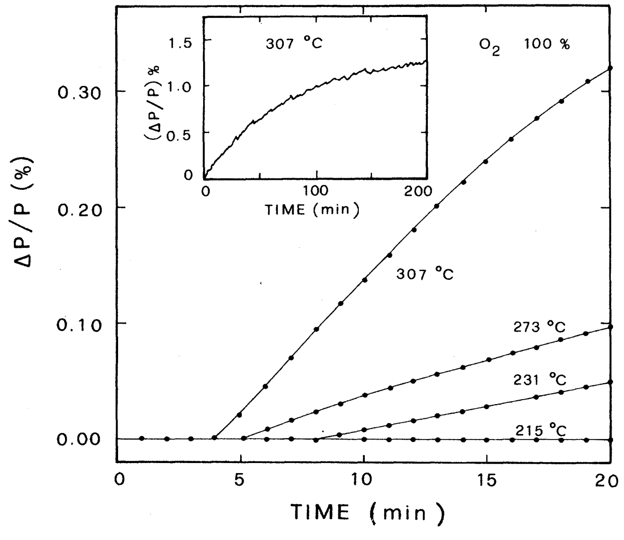

FIG. 2. Weight variation, in percents of the initial weight, as a function of the annealing time at various temperatures. The inset shows a full curve up to 200 min at 307 °C.

lowest considered temperature, 215 °C, the weight change was lower than the sensitivity of our experimental apparatus. The samples started at an oxygen content of $x = 0.65$, and the analysis times were not long enough for x to reach saturation. In fact (see inset of Fig. 2), in 200 min at 307 °C a steady-state value was not reached. Figure 3 shows a selected portion of the x-ray diffraction spectra obtained from a sample heated at 215 °C and quenched after 1, 11, and 140 min. For comparison the spectra of the samples as-received and after heating at 750 °C for 50 min in argon are also shown. The portions of the spectra which indicate a modification from the pure tetragonal phase are shaded. After only 1 min of treatment the peak at 46.2 was asymmetric; 140 min were enough to develop a peak in the position corresponding to a pure orthorhombic material. The analysis of the whole x-ray diffraction spectrum obtained from the sample quenched after 140 min allowed for the identification of the usual two phases. However, while for the tetragonal phase 10^{-3} Å was the precision in determining the lattice parameter, the resolution was at least 5 times lower for the orthorhombic phase. Although the low number of peaks, which can be unambiguously identified for the orthorhombic phase, were responsible for the lack of precision, the error and the shape of several peaks taken at high-diffraction angles suggested the presence of orthorhombic domains with a 90 ° misorientation.

A summary of the results obtained using various analytical techniques is reported in Table I. At room temperature the oxygen content was measured with nuclear reaction and the structure was determined with x-ray diffraction.

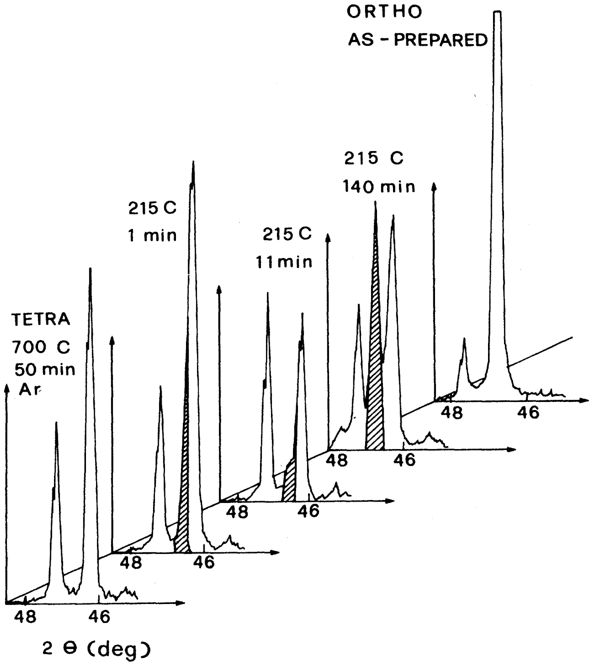

FIG. 3. Partial x-ray diffraction spectra taken from samples annealed at 215 °C and quenched after 1, 11, and 140 min of annealing at 215 °C. As a reference, the spectra from as-prepared, orthorhombic and annealed at 750 °C, tetragonal samples is also reported. The shaded area evidences the transformation.

For temperatures below ambient the resistance was measured on quenched samples and several representative data are reported in Fig. 4. The sheet resistance was not converted to resistivity due to the difficulty in defining the thickness of the layer which contributes to the conductivity. Two quantities are worthy of notice: the transition temperature and the value at room temperature of the sheet resistance. A general feature of our samples was that, when superconducting, the transition temperature was always around 90 K. The values of sheet resistance measured at room temperature are affected by the temperature and time of the heat treatment: 215 °C for 140

TABLE I. Summary of results for Y-Ba-Cu-O samples. The reported oxygen content was measured by nuclear reaction analysis.

Sample treatment	X-ray diffraction results	Low-temperature resistance	Oxygen content
As-prepared	Orthorhombic; $a=3.817$, $b=3.884$, $c=11.671$ (Å)	Metal; $T_c=91$ K	6.9
215 °C, 1 min	Tetragonal; $a=b=3.861$, $c=11.803$ (Å)	Semiconductor	6.4
215 °C, 11 min	Tetragonal; $a=b=3.858$, $c=11.810$ (Å)	Semiconductor	6.4
215 °C, 140 min	Orthorhombic; $a=3.820$, $b=3.890$, $c=11.714$ (Å) Tetragonal; $a=b=3.859$, $c=11.799$ (Å)	Metal; $T_c=89$ K	6.55
215 °C, 1000 min	Orthorhombic; $a=3.820$, $b=3.890$, $c=11.681$ (Å) Tetragonal; $a=b=3.859$, $c=11.811$ (Å)	Metal; $T_c=90$ K	6.6
273 °C, 200 min	Orthorhombic; $a=3.817$ $b=3.885$, $c=11.674$ (Å)	Metal; $T_c=90$ K	· · ·
700 °C, 50 min	Tetragonal; $a=b=3.861$, $c=11.810$ (Å)	Semiconductor	6.35

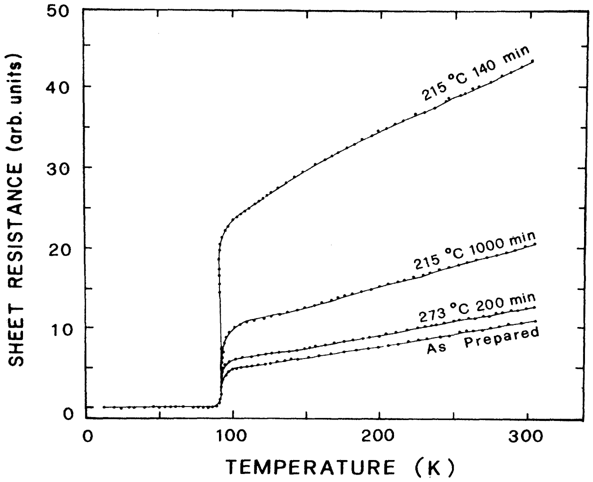

FIG. 4. Sheet resistance as a function of the temperature for samples heat treated at different times and temperatures.

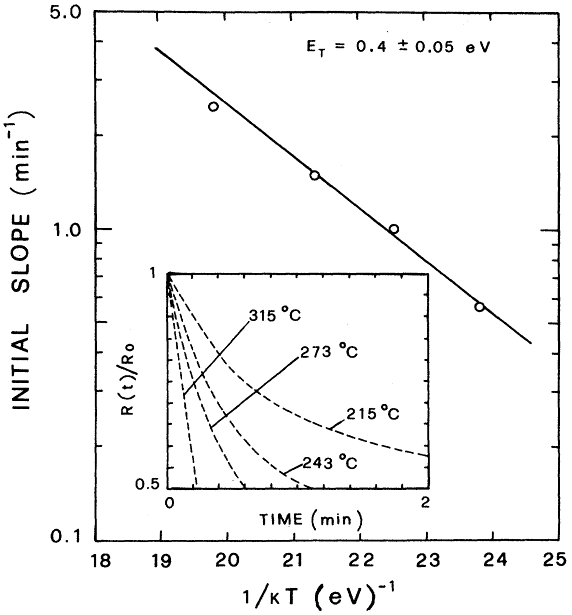

FIG. 5. Arrhenius plot of the initial slopes of the resistance vs time curves. The inset indicates the slopes.

min produced a sample with a room-temperature sheet resistance 2–3 times greater than that resulting from a treatment at 215 °C for 1000 min, and 4–5 times greater than the as-prepared samples.

DISCUSSION

The introduction of oxygen in the annealing ambient during the heat treatment of the tetragonal phase of the oxide produces, as in Fig. 1, a continuous decrease in resistance, rapid at the onset and sluggish after a certain time. Moreover, the sharp initial decrease is not associated with a measurable change in oxygen concentration (see Fig. 2); the oxygen content starts to increase only after a delay which decreases at increasing temperature.

The experimental evidence suggests that the presence of oxygen activates two processes, one very fast and the other with a much slower time constant. To characterize the processes the initial and the final slopes of the resistance curves plotted as a function of $1/kT$ (eV). The data points for the initial slopes plotted in Fig. 5 can be fitted with a straight line, suggesting a process in the considered temperature range controlled by a single mechanism having an activation energy of 0.40 ± 0.05 eV. The same kind of plot made for the final slopes yields an activation energy of 0.9 ± 0.1 eV, suggesting a different mechanism.

The physical phenomenon responsible for the initial decrease can be identified by analyzing the various possible mechanisms that effect the resistivity. It is pointed out again that the change in resistance occurs without an appreciable increase in the oxygen content and that although the x-ray diffraction from samples quenched from 215 °C after 1 and 11 min show the presence of only the tetragonal phase, the shapes of the peaks reveal a modification of the samples.

The resistivity in a material is determined by the product of carrier concentration and mobility. Measurements performed in the orthorhombic oxide as a function of time and temperature at various oxygen partial pressures[12–14] indicate that the carrier mobility is almost constant and that the density of hole carriers is modulated by oxygen doping. A similar analysis of tetragonal oxide has not yet been performed; however, in previous studies all the data points are unaffected by the change in structure, suggesting that in tetragonal material also the carrier concentration is associated with changes in resistance. Therefore we believe that the variation in sheet resistance is due mainly to the carrier concentration change and not to the scattering processes. It is worthwhile to remember that the presence of oxygen in this material is mandatory in order to promote the decrease of the resistance; a sample left overnight in Ar ambient does not appreciably change its resistance.

The presence of a continuous conductive skin surrounding the Y-Ba-Cu-O grains can be responsible for the observed variation; it has been estimated that a 500-Å thick film with $x = 0.1$ is enough to produce the change shown in Fig. 1. However, the presence of such a film should be detected by weight measurements and revealed by low-temperature resistance data. Another possible interpretation considers that the number of carriers is affected by the position of the oxygen atoms in the structure and not the quantity of oxygen. More precisely, charge carriers for conductivity originate in the oxygen atoms in $(0, \frac{1}{2}, 0)$ sites, while oxygen in the $(\frac{1}{2}, 0, 0)$ sites adds no carrier. At equilibrium, annealing at 700 °C in argon produces an order-disorder transition with $x = 0.65$ and the oxygen content in the excess of the pure tetragonal phase $(x = 1)$ is mostly located in the $(\frac{1}{2}, 0, 0)$ sites.[15] Very few carriers are available for conduction and the material is highly resistive. The annealing at low temperatures in the presence of oxygen promotes the disorder-order transition with the transfer of oxygen atoms from the $(\frac{1}{2}, 0, 0)$ site, where oxygen gives no additional carrier, to the position $(0, \frac{1}{2}, 0)$ where oxygen adds mobile charge carriers to the system. Few oxygen atoms are necessary to activate this process, and the oxygen atoms need only to move from one position to an adjacent one. This explains both why the oxygen content does not change appreciably as well as the relatively low value for the activation energy. The driving force for the process arrives from the fact that at low temperatures (below 600 °C) the probability of occupancy of the $(0, \frac{1}{2}, 0)$ sites is higher than that for the $(\frac{1}{2}, 0, 0)$ sites.

With increasing time the oxygen diffuses into the bulk and the decrease in resistance is due to massive introduction of oxygen in the material. The diffusion occurs in a material which is at least partially orthorhombic, and a possible schematic of the sample is a grain having a skin with an oxygen concentration higher than 6.8 and a much lower oxygen content inside. According to the data in the literature a material with such an oxygen content should have a T_c around 90 K. This picture is largely supported by the relatively small quantity of oxygen present, by the fact that the T_c is around 90 K, and by the high value of the resistance at room temperature. Even the data for the sample annealed at 215 °C for 140 min can be interpreted with this model. In fact, a skin of 1000 Å of Y-Ba-Cu-O with $x=0.2$ surrounding a grain of $30\times30\times10/\mu m^3$ with $x=0.6$ should give a negligible change of p, a T_c around 90 K due to filamentary conduction, the coexistence of orthorhombic and tetragonal phase, and a room-temperature resistance value higher than those measured on the as-prepared sample. Moreover, nuclear reaction analysis, which is a technique that is more surface sensitive than weight measurements, gives an increase in oxygen content. This picture is in agreement with recent published data obtained under comparable circumstances.[3,6]

In conclusion, we have shown that heat treatment of a tetragonal Y-Ba-Cu-O oxide in the presence of oxygen initially produces a large variation in resistance which can be attributed to the presence of a conduction skin or, more likely, to a relaxation of the structure of the disorder-order type. Subsequently, oxygen diffuses and the tetragonal Y-Ba-Cu-O grains are surrounded by a layer having orthorhombic structure and a transition temperature around 90 K.

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[1] R. J. Cava, B. Batlogg, A. P. Ramirez, D. Werder, C. H. Chen, E. A. Rietman, and S. M. Zahurak, Mater. Res. Soc. Symp. Proc. **99**, 19 (1988).

[2] Y. Kubo, Y. Nakabayashi, J. Tabuchi, T. Yoshitake, T. Manatko, A. Ochi, K. Utsumi, H. Igarashi, and M. Yonezawa, Mater. Res. Soc. Symp. Proc. **99**, 89 (1988).

[3] D. Shi, K. Zhang, and D. W. Capone II, J. Appl. Phys. **64**, 1995 (1988).

[4] D. Shi and D. W. Capone II, Appl. Phys. Lett. **53**, 159 (1988).

[5] D. Shi, D. W. Capone II, K. C. Goretta, K. Zhang, and G. T. Goudey, J. Appl. Phys. **63**, 5411 (1988).

[6] K. N. Tu, N. C. Yeh, S. I. Park, and C. C. Tsuei, Phys. Rev. B **38**, 5118 (1988).

[7] F. C. Matacotta, G. Nobile, G. Serrini, M. D. Giardina, and A. E. Merlini, Mater. Res. Soc. Symp. Proc. **99**, 561 (1988).

[8] L. C. Feldman and S. T. Picraux, in *Ion Beam Handbook for Material Analysis,* edited by J. W. Mayer and E. Rimini (Academic, New York, 1977), p. 109.

[9] F. Nava, O. Bisi, and K. N. Tu, Phys. Rev. B **34**, 6143 (1986).

[10] A. Alberti, J. Appl. Crystallogr. **9**, 373 (1976).

[11] G. Calestani and C. Rizzoli, Nature (London) **328**, 606 (1987).

[12] N. Karpe, I. Szymczak, D.-X. Chen, A. Sanchez, J. Nogues, and K. V. Rao, Mater. Res. Soc. Symp. Proc. **99**, 483 (1988).

[13] G. S. Grader, P. K. Gallagher, and A. T. Fiory, Phys. Rev. B **38**, 844 (1988).

[14] Y. H. Han and D. W. Monroe, Mater. Res. Soc. Symp. Proc. **99**, 753 (1988).

[15] J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, and I. K. Schuller, Phys. Rev. B **36**, 3608 (1987).