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X-ray irradiation as an improvement technique for oxygen ordering and enrichment of $YBa_2Cu_3O_{7-x}$ single crystals

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The effects of X-ray irradiation on as-grown $YBa_2Cu_3O_{7-x}$ single crystals were investigated, in order to test the effects of radiation-induced defects during the subsequent annealing in O_2, and to verify if short-circuits for diffusion could be provided that improve the oxygen enrichment of the specimens. X-ray irradiation was found to have a favourable effect on the homogeneity of the oxygen enrichment of the samples, as stated by the high reproducibility of resistance measurements carried out on specimens grown, irradiated and annealed under the same conditions. Even if X-ray irradiation seems unable to determine a significant reduction of the time needed for annealing, and it could not consequently be regarded as a totally resolutive step during the production of high-quality monocrystalline superconductors, the observed homogenization of lattice oxygen distribution seems to be exploitable. © *1998 Chapman & Hall*

1. Introduction

The flux method of crystal growth takes advantage of a low melting region of a subsystem of pseudo-ternary $BaO–CuO–Y_2O_3$ bounded by $BaCuO_2–CuO$ and $YBa_2Cu_3O_x$ (generally indicated as 1 2 3 phase) [1–6]. Crystallization occurs starting from the temperature of incongruent 1 2 3 phase decomposition to that of the ternary eutectic. Melting temperatures depend on partial pressures of oxygen, impurities in the source materials and solubility of crucible material in the melt [7–10].

However, in spite of major developments in crystallization techniques and growth process, there is a generally considerable variation in critical temperature obtained from different types of measurements. In particular, oxygen deficiency or inhomogeneity influence physical properties [11, 12]. This limitation is mainly due to the high stability of the oxygen poor, tetragonal phase at the elevated temperatures of crystallization [8].

Oxygen enrichment of the as-grown $YBa_2Cu_3O_{7-x}$ crystals can be obtained by annealing in O_2 at various low temperatures and different pressures, but very long times are normally required [11, 12]. Furthermore, no ordering of oxygen can be guaranteed at a microscopic level, because the state of the oxygen sublattice is strongly influenced by the entropy introduced in the single crystal during crystallization. Even if the variations of the oxygen content involve only the population and the depopulation of one oxygen site along the copper–oxygen chains, the distribution of the oxygen vacancies depend sensitively on the technique of material preparation [13], so that several different metastable microscopic oxygen arrangements in the region of copper chains may correspond to the same stoichiometry [14, 15]. For a given total oxygen content, the oxygen may be long- or short-range ordered, or disordered, and this may give rise to the differences observed in the structural parameters and the electronic behaviours of samples having the same value for oxygen deficiency. Finally, the temperature can have an influence also because of the strong anisotropy of the oxygen self-diffusion in the single crystal [16].

No kind of investigation has ever been carried out about the influence of defects created by irradiation on the behaviour of the oxygen-poor tetragonal phase during the usual annealing process of the as-grown crystals. It seems reasonable that these defects, whatever they can be, could act as short-circuit for diffusion of oxygen into the 1 2 3 phase, thus allowing for faster and more homogeneous oxygen enrichment.

Irradiation effects on oxide superconductors have been investigated by means of ions [17], electrons [18], protons [19] and other kinds of particles [20] to control the superconducting properties and to examine the physical characteristics of these materials. In particular it has been demonstrated that the irradiation with fast neutrons improves the flux pinning in high temperature superconducting (HTSC) materials. The most significant effects have been reported by Van Dover *et al.* in YBCO single crystals [21]. The radiation response of single crystals to fast neutrons is neither simple nor identical for all materials. On the other hand, irradiation with heavy particles, such as ions, primarily induces the mechanical damage, or destruction of crystalline structures, leading to the amorphization and to a change of the chemical composition of materials exposed [22]. On the other hand it is well known that the superconducting properties, in particular T_c and J_c, can be improved on YBCO thin films by laser irradiation [23]. These photoinduced changes in the transport properties have been explained in terms of photogeneration of charge carriers in the CuO_2 planes [24] and photoassisted oxygen ordering in the O(1)–O(5) plane [25, 26]. Therefore, photon irradiation of YBCO is a very interesting subject of investigation, considering the remarkable influence it has on the superconducting properties through the modifications it induces in the chemical state.

In this work YBCO single crystals were irradiated with X-ray emitted from a Mo X-ray tube; calculations and predictions have been made concerning the energy release for these and other radiations of different energy. X-ray can excite electrons in the CuO bonds, inducing photochemical reactions in the single crystal. Oxygen vacancies may be created in the Cu–O planes and chains, since oxygen atoms are removed from their original sites and excited electrons relaxed to locate on Cu sites. The oxygen vacancies could be filled by the oxygen annealing at relatively low temperature (400–500 °C). On the other hand, cations are primarily fixed, because X-ray photons are unable to induce the ejection of cations.

2. Experimental procedure

2.1. Growth of single crystals of the 1 2 3 phase

Single crystals of the 1 2 3 phase have been grown by the flux method from a melt of non-stoichiometric composition in the pseudoternary system Y_2O_3, BaO, CuO. 10 wt% of YBCO powders was added to BaO_2 and CuO previously mixed in a ratio of Ba:Cu = 28:72, corresponding to a eutectic in the diagram BaO–CuO. The powdered mixture was sieved repeatedly, placed in an Al_2O_3 crucible Alsint 99.7 (about 20 g for each run), and then melted in a vertical furnace Carbolite TZF 12/100. The temperature was raised up to a maximum of 1005 ± 2 °C in air at a rate of 200 °C h^{-1} and maintained for 24 h in order to guarantee a complete homogenization of the melt. Higher temperatures were found to be detrimental, both because of the thermal instability of YBCO, and of the creeping of the melt on crucible walls at about 1020 °C.

The system was then cooled down to 930 ± 2 °C at 1.5 °C h^{-1}. The residual flux was sucked by dipping in the crucible a porous piece of sintered MgO. Having withdrawn the wick and after laying it on an alumina plate near the crucible, the temperature was lowered to 450 ± 1 °C at different rates up to 10 °C h^{-1}. The furnace was then free-cooled to room temperature in about 12 h.

Free single crystals of size $5 \times 5 \times 0.2$ mm^3 were easily recovered both from the crucible and from the wick surface.

The structure of the samples was determined by an X-ray diffractometer (XRD) Philips PW 1710, both on single crystals and on powders obtained by grinding some crystals, using CuK_α radiation.

The oxygen content was determined from lattice parameters. Other methods such as iodometric titration and thermogravimetry were tested but they were found to be less reproducible and more inaccurate because of the scarce amount of the specimens; moreover they require the destruction of the crystals.

The aluminium content of the samples was determined by dissolving some crystals in hydrochloric acid at different concentrations; the solutions obtained were analysed by an AA spectrometer Varian 1725, on a flame N_2O–C_2H_2, and by a plasma spectrometer Jobin Yvon J24. Both the instruments revealed an aluminium content lower than 1 at %.

2.2. Irradiation of the as-cast samples

Some of the as-cast crystals were placed on an appropriate support at the centre of a common Debye chamber, and exposed for 20 h to the non-filtered X-ray beam of a Mo anticathode, working under a tension of 37 kV and at a current of 37 mA, at a distance of 110 mm from the source.

The exposure/time curve was determined by thermoluminescence dosimetry (TLD), using LiF 100 TLDs placed at the same distance as the specimens from the anticathode. The dosimeters were read by an Harshaw/TLD System-4000 photometer.

The dependence of the exposure on time was linear

$$X = 64.97t + 2.77 \qquad (1)$$

where X is the exposure in roentgen and t the time in seconds, with a correlation coefficient of 0.999.

The exposure was converted into the adsorbed dose D by applying the equation

$$D = X 0.873 \frac{(\mu/\rho)_{\mathrm{YBCO}}}{(\mu/\rho)_{\mathrm{air}}} \qquad (2)$$

where the mass attenuation coefficient of the 1 2 3 phase $(\mu/\rho)_{\mathrm{YBCO}}$ at 17.4 keV (MoK_α energy) was evaluated as the sum of the analogous coefficients for the compounding elements at the same energy, each of them multiplied by the corresponding weight fraction in the compound [27]. The dose adsorbed in 20 h was evaluated to be 1.5×10^6 Gy.

Irradiation created a remarkable number of surface defects, visible with an optical microscope and placed along the traces of the lamellar growth (see Fig. 1). Somewhere on the surface, the crystals appeared quite

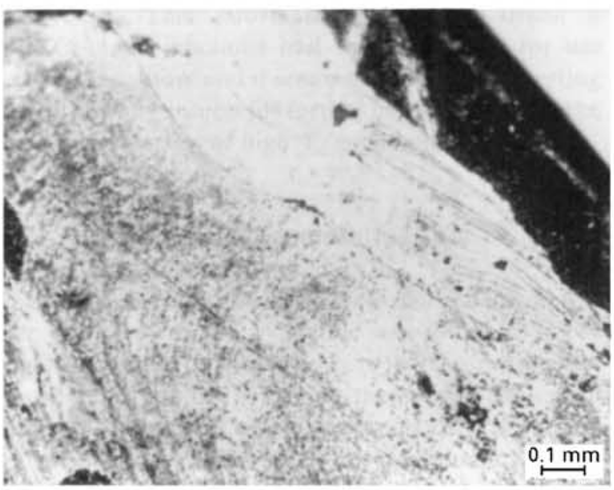

Figure 1 Optical microscopic view of an irradiated crystal (marker indicate 0.1 mm). Surface defects created by irradiation are concentrated along the lamellae of growth.

broken up. This desegregation has been found to involve the whole surface for doses $D > 6 \times 10^6$ Gy.

2.3. Annealing

Both the as-cast and the irradiated crystals were annealed for 48 h in flowing oxygen at a temperature of $450 \pm 1\,^{\circ}\mathrm{C}$. Heating and cooling rates to and from 450 °C were $120\,^{\circ}\mathrm{C\,h^{-1}}$.

If compared with data reported in literature [28, 29], the anneal was short, and it was not expected to produce good superconducting properties. It was, however, long enough to reveal if irradiation can play role in activating the crystal surface, thus improving the final quality of annealed products.

2.4. Resistance measurements

The electrical resistance of the annealed crystals was measured by the standard four-probe technique, in the temperature range from 300 to 10.5 K, measured by a Au–Fe 0.7%/Chromel thermocouple.

High-quality contacts (high mechanical resistance, low contact resistivity) were easily provided on not irradiated crystals by welding Cu wires on the surface (*ab* plane) with In. Pure In did not wet irradiated YBCO, but In–Ag 3 at % alloy provided good quality contacts. Like In on irradiated crystals, this alloy does not show high wettability on non-irradiated YBCO; this suggests that something more complex than a simple mechanical desegregation is provided by irradiation.

3. Results and discussion

3.1. Structural analysis and oxygen content

None of as-cast crystals was found to have orthorhombic structure. XRD patterns from powders obtained by grinding some crystals showed the characteristic peaks of the tetragonal one (Fig. 2a), but some anomalies (Fig. 2b) in the height and position of peaks were observed which can be explained by inhomogeneity in the oxygen content or ordering in different crystals, or by a partial orientation of grains in the powders.

A more accurate determination of oxygen content was obtained by calculation of lattice parameters. Much work is available to correlate these data (see for instance ref. 30). Two methods were used: (i) the evaluation of a, b and c parameters from powder data collection, to get to a mean value of the oxygen content in a batch of crystals obtained from the same thermal treatment; (ii) the evaluation of the c parameter from 0 0 1 reflection positions to determine the amount of oxygen in a large single crystal. In this case the c value was calculated by a linear extrapolation of the lattice parameter versus reflection angle 2θ using the Nelson–Riley correction function [31]. The second method was necessary to verify changes in the oxygen content of a single crystal after annealing, irradiation, or both treatments.

The results of these calculations can be summarized as follows. The oxygen content of as-cast single crystals was between 6.35 and 6.60, depending on the cooling rate after the flux suction; resistance measurements performed on an as-cast crystal (Fig. 3) confirmed that its oxygen stoichiometry was significantly far from 7.00. A marked increase in normal-state resistance was observed when approaching the transition to the superconducting state, indicating a severe deficiency and unhomogeneity in the oxygen content of the specimen [32, 33]. The oxygen content of annealed, non-irradiated or irradiated crystals, increases generally from about 6.55 to 6.70, achieving a maximum of 6.76 in the case of a sample irradiated and annealed. The XRD pattern of powders obtained from this sample is shown in Fig. 4. The orthorhombic structure due to the high oxygen content was confirmed by the appearance of the 0 1 3 peak on the left of the 1 1 0 peak, which overlaps with 1 0 3 at $2\theta \cong 32^{\circ}$ (see insert).

3.2. Irradiation

Being that the oxygen content of the as-grown crystals was quite low as discussed above, a stoichiometry $YBa_2Cu_3O_{6.5}$ was assumed to calculate the energy release for different radiations. The attenuation in a thickness x of YBCO was then evaluated according to the equation

$$I(x) = I_0 \exp(-x\mu_{\mathrm{YBCO}}) \qquad (3)$$

where I_0 is the intensity at $x = 0$, $\mu_{\mathrm{YBCO}} = \rho_{\mathrm{YBCO}}(\mu/\rho)_{\mathrm{YBCO}}$ and ρ_{YBCO} is the density of $YBa_2Cu_3O_{6.5}$ in $\mathrm{g\,cm^{-3}}$. Results are given in Table I.

TABLE I Mass attenuation coefficient of $YBa_2Cu_3O_{6.5}$ and expected attenuation for radiations for selected sources

Radiation	Source	Energy (KeV)	μ_{YBCO} ($\mathrm{cm^{-1}}$)	Attenuation % in 0.1 mm of YBCO
γ	$^{60}_{1}$CO	1300	4×10^{-3}	0.3
X	K_{α}Fe	6.4	2016	~ 100
X	K_{α}Cu	8.9	1096	~ 100
X	K_{α}Mo	17.4	285	85

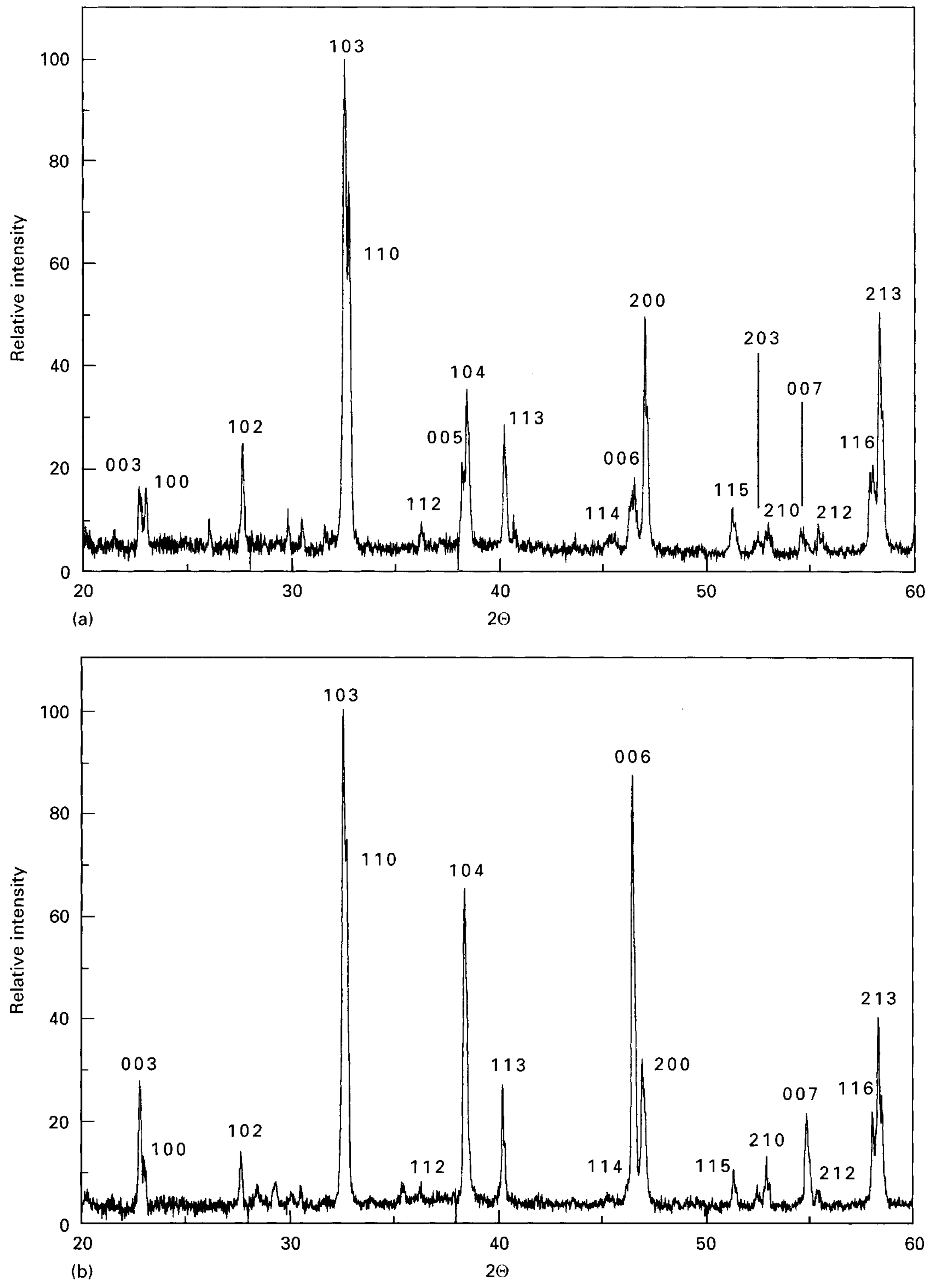

Figure 2 XRD patterns for powders obtained by crumbling some crystals. (a) These crystals were fast-cooled from 930 °C to ambient temperature: they show evidence of tetragonal structure. (b) These crystals were slow-cooled from 930 °C to ambient temperature: they show some anomalies in the height and position of peaks, particularly the 006 and 200 reflections at $2\theta \cong 46°$.

Just a small amount of energy is expected to be released by γ rays due to their high mean free path in matter. This result could explain the remarkable resistance of the superconducting properties of $YBa_2Cu_3O_{7-x}$ and $REBa_2Cu_3O_{7-x}$ to γ irradiation, which has been observed by different authors [34–36].

On the contrary, X-rays are expected to release a significant amount of energy in a limited thickness, creating damage and defects. Enokihara *et al.* have observed that X-rays are capable of destroying superconductivity in $ErBa_2Cu_3O_{7-x}$ [22]. In particular Mo X-rays used in the present work have a significantly high energy, and are consequently expected to create a significant damage, together with a considerable high attenuation coefficient.

As described in the previous sections, the damaging of the samples by the radiation was evident even under optical microscopic observation; moreover, the different wetting behaviour of irradiated samples with respect to non-irradiated specimens leads us to conclude that some kind of chemical, electronic and structural re-organization takes place under the action of the X-ray. This information could be useful if YBCO–metal junctions had to be designed for use under irradiation, and it seems to be a very interesting and promising subject for further investigations on the general properties of high T_c superconductors.

3.3. Annealing and resistance measurements

Even after annealing in oxygen, neither the irradiated, nor the non-irradiated crystals was found to super conduct above 70 K, or to show a transition onset above 85 K; this confirms that the oxygen content of all the specimens was still low with respect to that of the highest temperature superconducting phase $YBa_2Cu_3O_{7-x}$ with $x < 0.2$. Thus surface defects apparently do not assist in reducing the time required for annealing. On the contrary, X-ray irradiation was found to have remarkable consequences on the homogeneity of the oxygen content of the samples, both as-cast and after annealing in oxygen.

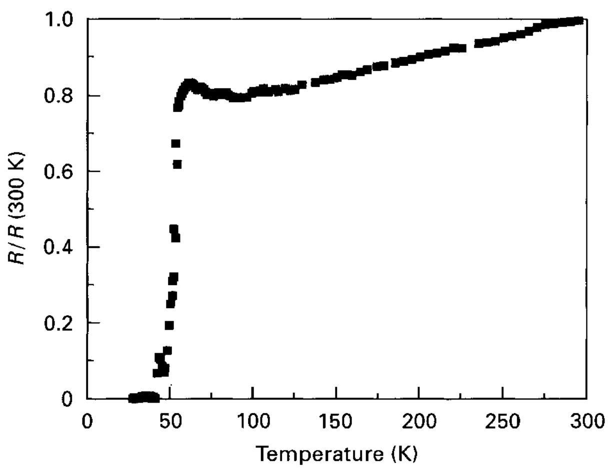

Figure 3 Resistance normalized to resistance at 300 K against temperature, measured on an as-cast crystal.

As previously discussed, different researchers have observed that oxygen annealing of as-grown crystals frequently gives irreproducible results, unless the annealing is conducted for several days [28, 29]. This has been confirmed in this work.

The measured value of electrical resistance R normalized with respect to the corresponding values at ambient temperature, R (300 K), are plotted against temperature in Fig. 5a and b for two non-irradiated crystals. The two profiles differ significantly, although both the samples have been grown and annealed under the same conditions. None of the non-irradiated crystals completes the transition in a temperature range narrower than 20 K. Furthermore, Fig. 5b shows the change from metallic to semiconductor-type behaviour already observed in the as-cast samples, indicating a significant oxygen deficiency, as discussed above. In contrast, crystals which have been irradiated before annealing in O_2 showed a much more homogeneous behaviour when resistance measurements were performed under identical conditions. Results are shown in Fig. 6a, b and c. Even if the critical temperature is low, the semiconductor-type behaviour of normal-state resistivity disappears in all cases; the value of R/R (300 K) uniformly decreases from ambient temperature to the point of transition onset; in two cases (Fig. 6b and c) the transition takes place in a relatively narrow range of temperature. Finally, a very low resistance in the normal state is observed at least in one irradiated crystal (Fig. 6c) just before the transition to the superconducting state. The data indicates that the quality of YBCO

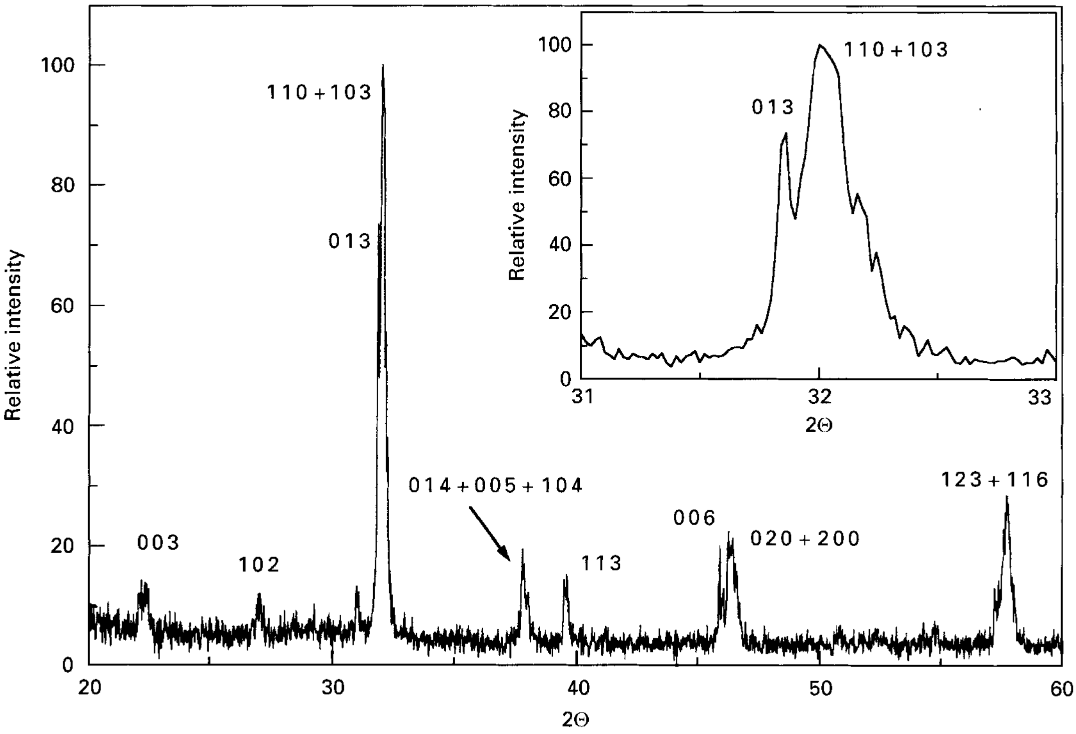

Figure 4 XRD pattern for powders obtained by crumbling an irradiated and annealed single crystal.

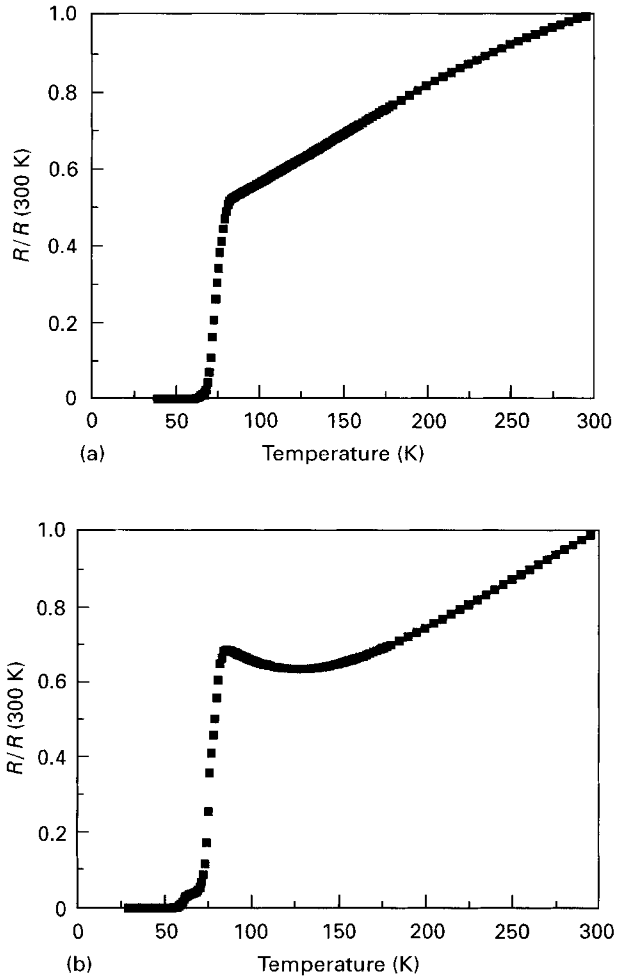

Figure 5 Resistance normalized to resistance at 300 K against temperature, measured on two different non-irradiated $YBa_2Cu_3O_{7-x}$ single crystals annealed in flowing oxygen for 48 h. The two curves differ significantly: (a) shows a metallic behavior in the normal state, while (b) shows semiconducting behaviour.

single-crystals can be significantly improved by irradiating the as-cast specimens before oxygen annealing.

In order to confirm these observations, a large platelet crystal (6 × 6 × 0.4 mm^3) was divided in three sections. Two of them were X-ray irradiated, and only one submitted to subsequent annealing together with the third section; both irradiation and annealing procedures were the same as described in previous sections. The electrical resistance of the three sections was then measured and the results are presented in Fig. 7, together with the R/R (300 K) profile of the as-cast, non-irradiated specimen of Fig. 3. Two effects are clearly visible. The first is that the oxygen annealing displaces the superconducting transition towards higher temperatures; the second important effect is that irradiation modifies substantially the resistance profile in the normal state, both in the annealed and in the as-grown crystals. The semiconductor-type behaviour in normal state, which is a predominant feature of the non-irradiated specimens, practically disappears in the irradiated ones, showing that the homogeneity of the samples with regard to their oxygen content is definitely improved by irradiation. In particular, a more detailed comparison can be made between the annealed crystals, which are, as described previously, different sections of the same platelet. A valuable smoothing of the curve in the transition region is observed due to irradiation, even if a marked lack of continuity in the derivative of R/R (300 K) versus T still remains, so that just a little narrowing of the transition as a whole is obtained. From this point of view, irradiation did not produce results as satisfactory as in the cases reported in Figs 6a, b and c. This is

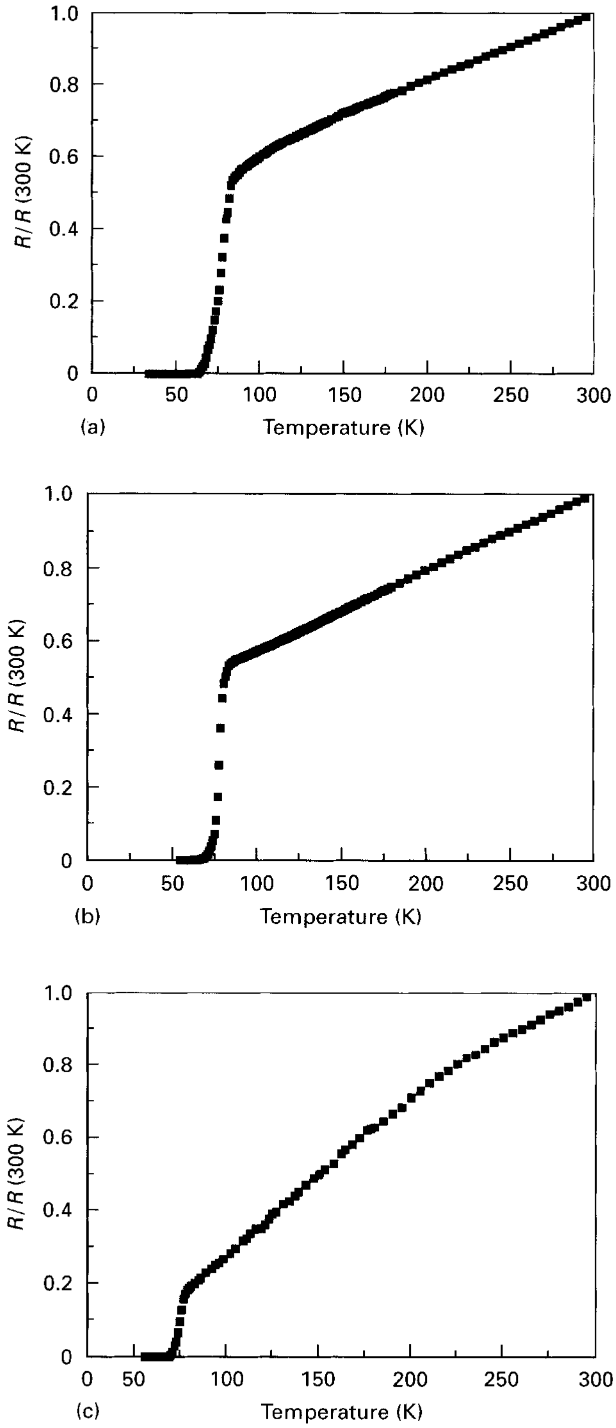

Figure 6 Resistance normalized to resistance at 300 K against temperature, measured on three different X-ray irradiated $YBa_2Cu_3O_{7-x}$ single crystals annealed in flowing oxygen for 48 h. All three curves show a metallic behaviour in the normal state; the transition range narrows from (a) to (c).

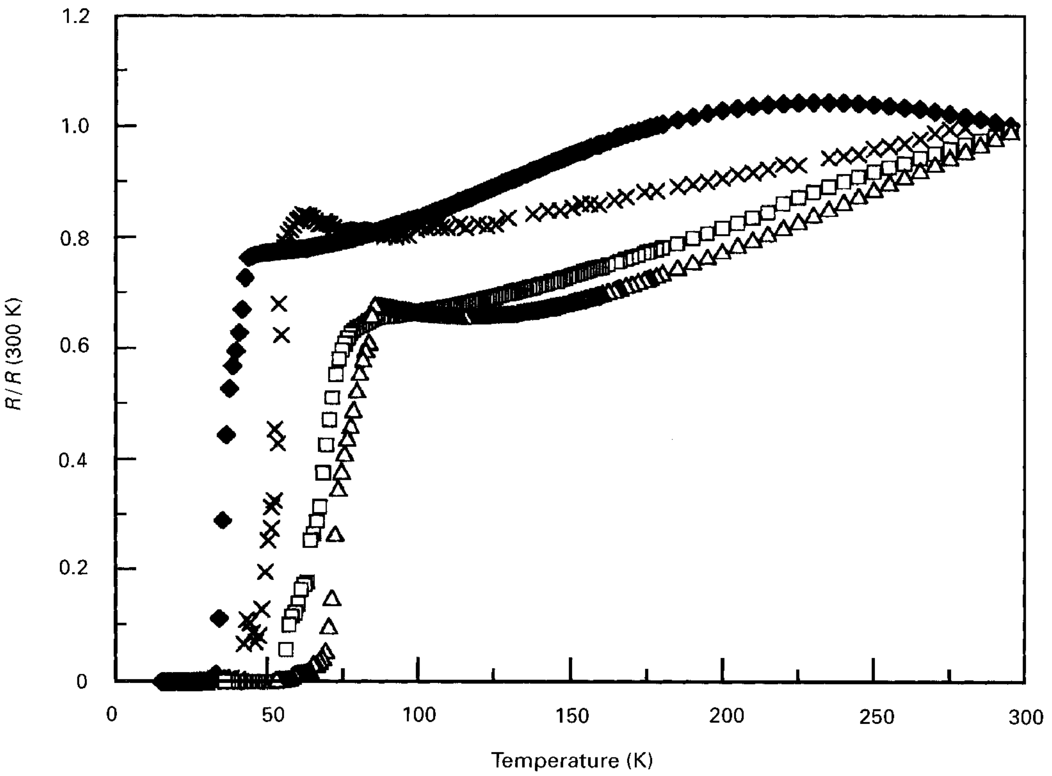

Figure 7 Resistance normalized to resistance at 300 K against temperature, measured on three different sections of the same $YBa_2Cu_3O_{7-x}$ single crystal treated in different conditions, compared with an as-cast specimen. (×) as-grown crystal; (◆) irradiated, non-annealed (△) non-irradiated, annealed; (□) irradiated, annealed.

probably due to the thickness of this last platelet, which was greater than that of the samples used for other experiments, as required by the necessity to divide it in sections. As a consequence of the different dimensions along the *c* axis, the annealing times required to obtain the same results reported for the other irradiated specimens would probably be longer than those used here.

If X-ray irradiation was followed by a long-lasting annealing, the final quality of superconductors should be better than that obtained by just heating the as-cast crystals under flowing O_2. It can also be supposed that other kinds of radiation may be able to provide results even better than X rays. Even if the utilization of γ rays seems not advisable, β particles and/or accelerated electrons should determine modifications both on the surface and in the bulk of the as grown crystals, may be favourable to high T_c superconductivity.

4. Conclusions

The effects of X-ray irradiation on as-grown $YBa_2Cu_3O_{7-x}$ single crystals were investigated, in order to test the effects of radiation-induced defects during the subsequent annealing in O_2, and to verify if short-circuits for diffusion could be provided that improve the oxygen enrichment of the 1 2 3 phase.

The radiation of a Mo anticathode was used as a source of X-ray, and significant alterations of the specimens were observed after irradiation, both by microscopic observation and through the modification of some fundamental physical properties such as the surface wettability by liquid solders.

X-ray irradiation was found to have a favourable effect on the homogeneity in the oxygen content of the samples, as stated by the high reproducibility of resistance measurements carried out on specimens grown, irradiated and annealed under the same conditions.

Even if X-ray irradiation seems unable to produce a significant shortening of the time needed for annealing, and it could not consequently be regarded as a totally resolutive step during the production of high-quality monocrystalline superconductors, this observed valuable power of homogenization of lattice oxygen distribution seems to be exploitable.

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