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Thermal annealing-induced ageing and structural effects in $YBa_2Cu_3O_{7-\delta}$ superconductors

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The $YBa_2Cu_3O_{7-\delta}$ superconductor loses part of its oxygen by thermal annealing, effectively at annealing temperatures $T_a \geqslant 400\,^\circ C$, under reduced air pressure. The release of the oxygen decreases monotonically as a function of time, at given T_a, and presents two different slopes; fast at the beginning and slow later. The initial slopes (dM/dt) of the isothermal mass loss curves, measured at different T_a, follow a straight line, as $\ln(dM/dt)$ is plotted against the T_a^{-1} (K^{-1}), suggesting the release of the oxygen to be a kinetic process with an activation energy $Q_1 = 0.45$ eV. The oxygen vacancies probably reside along the central-cage Cu–O chains, replacing O(4) ions, which break up spinal Cu–O linkages, and consequently the high T_c superconductivity properties suffer. A $YBa_2Cu_3O_7$ sample annealed for 30 min at 600 °C (at 10 mbar air pressure) thus gives a considerably reduced T_c at ~ 50 K, compared to 91 K without annealing. However, annealing, peculiarly at a higher $T_a \sim 700\,^\circ C$, for a short period of 10 min, has little effect on the high T_c appearing at ~ 70 K. We believe that the oxygen vacancies possibly populate on O(1) sites along the side Cu–O chains, at this particular temperature, and become positively charged on trapping the hole, thus helping the superconductivity.

1. Introduction

The in- and out-diffusion processes and the oxygen content are the intrinsic factors which shape the crystalline structure of $YBa_2Cu_3O_{7-\delta}$ with an orthorhombic or tetragonal crystal system or lead to the orthorhombic$\rightleftharpoons$tetragonal structural phase transformation, subject to thermal annealing at elevated temperatures, and thus control the high T_c superconductivity properties in the orthorhombic phase [1–8]. The control of these processes, on the basis of oxygen diffusion in the oxide, is mandatory in order to obtain a thermally stable material with reproducible and reliable characteristics. The oxygen in-diffusion in the tetragonal $YBa_2Cu_3O_{7-\delta}$ phase and the relationship between the oxygen content, δ, transition temperature T_c, and the tetragonal to orthorhombic structural transformation, have been reported [1–5], and more recently Ottaviani *et al.* [7, 8] have studied the effects on the electrical resistivity. The tetragonal–orthorhombic transformation occurs in oxygen ambient in the 200–700 °C temperature range and is kinetically controlled.

Tu *et al.* [6] studied the oxygen in-diffusion in orthorhombic $YBa_2Cu_3O_{7-\delta}$ ($\delta = 0.4$) with *in situ* resistance measurements, and concluded that the oxygen transport occurs through two different mechanisms characterized by the activation energies: (i) $Q_1 = 0.48$ eV, at $\delta = 0.38$; (ii) $Q_2 = 1.1$ eV, at $\delta = 0$. The origin of these mechanisms is not understood, further systematic research being required on oxygen diffusion in $YBa_2Cu_3O_7$ and similar other oxide superconductors in different atmospheres. Therefore, we performed a detailed thermogravimetric study of orthorhombic $YBa_2Cu_3O_7$ by heating it in air at a reduced pressure of 10 mbar. It was observed that the specimen readily lost a substantial portion of the oxygen, effectively at $T_a \sim 400\,^\circ C$ or higher. The release of the oxygen increases with increasing T_a and also reveals two different slopes, as measured as a function of time, supporting the presence of two different mechanisms for the oxygen out-diffusion from the $YBa_2Cu_3O_7$ structure. The preliminary results are reported in the present paper. X-ray diffractometry was utilized to study the effects of the oxygen out-diffusion on the $YBa_2Cu_3O_7$ crystalline structure. The results are correlated with the superconductivity properties.

2. Experimental procedure

The sample $YBa_2Cu_3O_{7-\delta}$, with $\delta \sim 0$, was prepared by sintering the stoichiometric composition containing Y_2O_3, $BaCO_3$ and CuO powders (after calcining at 950 °C for 12 h and then pressing into pellets) at 950 °C for 12 h followed by 2 h at 600 °C in an oxygen gas flow (250 $cm^3\,min^{-1}$). The crystalline structure of the product was analysed by X-ray diffractometry (XRD) using filtered CrK_α radiation and the lattice

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parameters were determined by a least-squares best-fit procedure. More than 20 characteristic diffraction lines of orthorhombic $YBa_2Cu_3O_{7-\delta}$ phase were analysed with an estimated standard deviation of 0.0005 nm.

Thermogravimetric measurements were performed using a Netzsch STA 409 thermogravimeter system, where 500 mg pure $YBa_2Cu_3O_7$ sample in a platinum capsule were heated at the predetermined T_a temperature under 10 mbar air pressure. In this experiment the sample was heated rapidly at 120 °C min^{-1} to the desired T_a and held, and the air pressure at the sample was reduced to ~ 10 mbar through an efficient vacuum system. The isothermal loss in mass in the sample was scanned against the time, t. All these measurements were controlled by a computer system.

The thermogravimetric system had sensitivity to detect the variation in mass of sample, of better than 0.01 mg, which allowed study of the loss of oxygen content, δ, in $YBa_2Cu_3O_{7-\delta}$, during heating, by scanning the mass of the sample as a function of time at a given temperature.

3. Results and discussion

3.1. Thermal annealing-induced effects

The $YBa_2Cu_3O_7$ loses part of the oxygen when heated under a reduced air pressure. Fig. 1 thus shows the loss in mass of a $YBa_2Cu_3O_7$ sample during heating, under a reduced air pressure of 10 mbar, at several different temperatures. The release of the mass decreases monotonically as a function of time, at a given T_a, which presented two different slopes (indicating two different desorption steps of oxygen) and an inflection point in between the two desorption regions.

The release of oxygen from the $YBa_2Cu_3O_7$ appears to be kinetically controlled by the T_a temperature and the air pressure in the closed column. This can be represented qualitatively by writing for the rate of release of the mass, during an isothermal annealing at T_a

$$\left(\frac{dM}{dt}\right)_{T_a} = M_0 \exp\left[-\left(\frac{Q_1 + Q_2}{kT}\right)\right] \times \exp\left[-(t/\tau)^{\beta}\right] \qquad (1)$$

where M_0 is the mass of the sample before given any annealing treatments, Q_1 and Q_2 are the activation energies characterizing the two desorption processes of the oxygen, and k is the Boltzmann constant. The second exponential term, i.e. $\exp[-(t/\tau)^{\beta}]$ in Equation 1, represents the structural relaxations in the system with the parameters τ as the induction period and β an exponent, usually assumed to be $\leqslant 1$ in modelling most relaxation processes [9, 10]. It is believed that the $YBa_2Cu_3O_7$ synthesized by the usual ceramic process occupies an energy state, E_1, which is significantly higher than the state, E_0, of the lowest energy admissible by the system. The sample therefore releases the excess ($\Delta E = E_1 - E_0$) structural energy, during the post-thermal annealing, as the E_0 energy state is approached. The phenomenon is usually called the "structural relaxation". The relaxation activated by the thermal annealing under a reduced air pressure induces redistribution of the oxygen vacancies among the probable sites in the $YBa_2Cu_3O_{7-\delta}$ crystal lattice, which in turn partly releases the oxygen from the lattice structure.

In order to characterize the oxygen out-diffusion process in $YBa_2Cu_3O_7$, we analysed the slopes of the isothermal mass release curves, given in Fig. 1, as a function of $1/T_a$. The data points for the initial parts of the curves (T_a < 850 K) fit a straight line well, the slope of which gives an activation energy Q = 0.45 eV (Fig. 2). A similar analysis using the slopes on the slower parts of the isothermal mass release curves of Fig. 1, is not reliably possible, because the variation in the data points is insignificantly small. However, it does indicate a different oxygen diffusion process from that represented by the initial part of the curves. Two different oxygen diffusion processes were also realized for the oxygen in-diffusion in tetragonal $YBa_2Cu_3O_{7-\delta}$ (δ ~ 0.65) from *in situ* resistance measurements [7, 8]. In that case the activation energy for the oxygen in-diffusion during the initial periods of

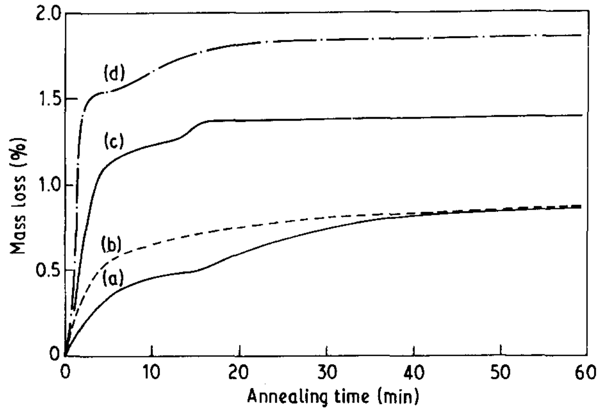

Figure 1 Mass loss (%) during isothermal annealing of $YBa_2Cu_3O_7$ superconductor at (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C under a reduced air pressure of 10 mbar. A fresh sample was used in each case.

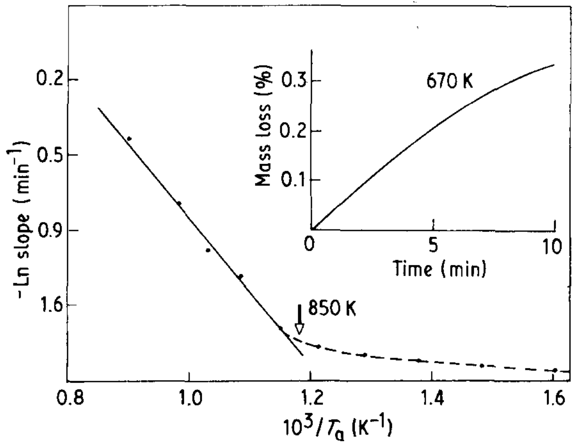

Figure 2 Plot of the initial slopes (logarthimic) of the isothermal mass loss curves, obtained by annealing $YBa_2Cu_3O_7$ at different temperatures (10 mbar), as a function of the inverse of the annealing temperature, T_a. The variation is represented well by the approximation of a straight line, which gives a slope Q_1 = 0.45 eV, for $T_a \geqslant$ 850 K. The slope of the isothermal mass loss curves (· · ·) decreases exponentially with T_a below 850 K. The initial part of the mass loss curve obtained during heating at 670 K is shown in the inset.

annealing was found to be 0.4 eV, which is fairly consistent with the value of 0.45 eV obtained from our thermogravimetric analysis of oxygen diffusion in orthorhombic $YBa_2Cu_3O_{7-\delta}$ at $\delta \sim 0$. Tu et al. [6] also estimated a similar value of 0.48 eV for the activation energy of the oxygen in-diffusion in the orthorhombic $YBa_2Cu_3O_{7-\delta}$, at $\delta \sim 0.38$, by *in situ* resistance measurements. A close similarity in the values of activation energies for the oxygen in- or out-diffusion, determined by the two different methods, confirms that the diffusion of oxygen in $YBa_2Cu_3O_{7-\delta}$ oxide is essentially reversible. Both the in- and out-diffusion processes are governed by similar structural parameters (which, in fact, are not known), within the limits for $\delta \leqslant 0.65$, irrespective of the crystal structure, i.e. no matter whether it is orthorhombic or a tetragonal.

The inflection point observed in between the two desorption regions of the oxygen in the isothermal mass release curves indicates almost no release of oxygen occurs during the annealing in this time interval. The crystalline state attained in the first oxygen desorption step probably undergoes a structural relaxation, on continuing the annealing, which causes configurational changes and ordering of the oxygen vacancies within the crystal lattice, thus minimizing the structural energy of the system. Isothermal treatment of the tetragonal $YBa_2Cu_3O_{7-\delta}$ at an effectively lower T_a (215 °C) in an oxygen atmosphere also does not exhibit any significant change in the oxygen content, but the electrical resistivity decreased monotonically as a function of the annealing time [7, 8]. We believe that both these features are intrinsic to the structural relaxation. Resistivity in this region is very sensitive to small change in oxygen content.

Fig. 3 shows the results of the electrical resistivity for the different annealed samples under a reduced air pressure of ~ 10 mbar. The annealing at $T_a \sim 600$ °C for 30 min effectively destroyed the high T_c superconductivity properties and the T_c was lowered (from 91 K) at ~ 50 K. However, peculiarly, the annealing at ~ 700 °C, for a short period of 10 min, does not greatly alter the high T_c characteristics, with T_c at ~ 70 K, which was found to be reproducible within experimental error. The other samples annealed for longer periods at $T_a \sim 700$ °C or at a higher T_a usually behave as semiconductors.

3.2. Effects of thermal annealing on XRD

Thermal annealing of $YBa_2Cu_3O_7$ at elevated temperatures reflects remarkable changes in the peak

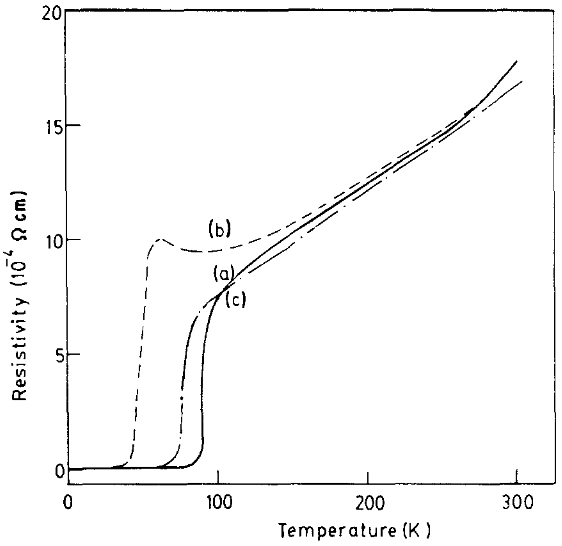

Figure 3 Electrical resistivity of $YBa_2Cu_3O_{7-\delta}$ measured as a function of temperature. (a) An as-prepared sample; (b, c) obtained after annealing the as-prepared sample (a) at (b) 600 °C for 30 min, and (c) 700 °C for 10 min.

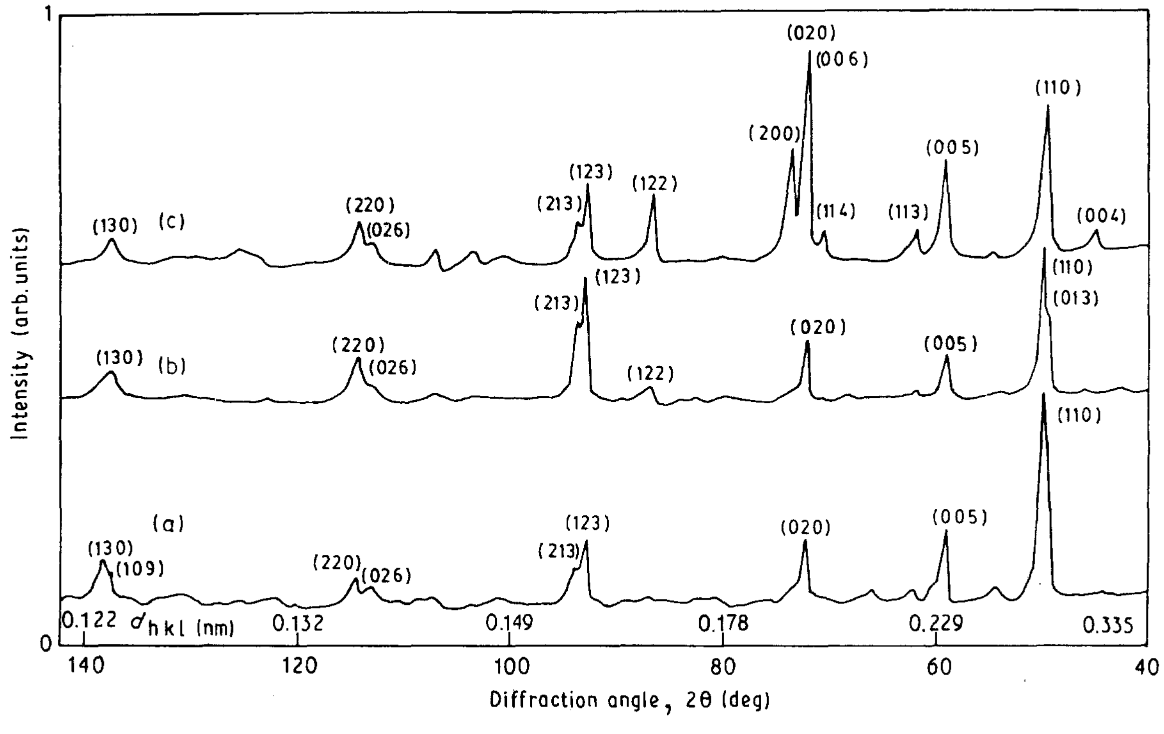

Figure 4 XRD patterns of (a) as-prepared $YBa_2Cu_3O_7$ sample, which was subsequently (b) annealed at 600 °C for 30 min, and (c) annealed at 800 °C for 20 min.

positions, intensities and half-bandwidths of the characteristic XRD peaks as can be seen from the diffractograms shown in Fig. 4. For example, the peak at (1 1 0) is the most intense one in the diffractogram (Fig. 4a) of the as-prepared $YBa_2Cu_3O_7$ sample, whereas the peaks at (1 2 3) and (0 2 0), were found to be the most or second-most intense peaks after annealing at 600 and 800 °C, for 30 min, Fig. 4b and c, respectively. Two additional peaks at (1 1 4) and (2 0 0) also appeared after annealing, particularly at high $T_a = 800\,°C$. The diffractograms displayed on a rather expanded scale of 2θ, (a) 48°–51°, and (b) 71°–74° in Fig. 5, summarize the effects of the thermal annealing of the half-bandwidths.

It should be pointed out that the $YBa_2Cu_3O_{7-\delta}$ obtained by an ordinary sintering process comprises a wide variation of grain sizes [11]. Irregular variation in grain sizes often disrupts smooth surfaces of the grains with voids, which causes broadening in the XRD peaks. Annealing of the sample at a suitable temperature allows the grains to smooth their surfaces by releasing excess structural energy, if any, and in turn modifies the microstructure of the interface between the grains and adjacent grain-boundary phases. In our experiments, the annealing at 700 or 800 °C thus eventually presented very sharp diffraction peaks (Fig. 5) due to the formation of sufficient smooth grain surfaces in those cases. Control of these structural defects by annealing may improve the superconductivity properties of the product. Similar results are also expected by crystallizing the ceramic grains in the presence of a suitable nucleation catalyst, preferably with a low melting temperature. We have been able to prepare $YBa_2Cu_3O_{7-\delta}$ ceramic superconductors using a ~ 2 mol% Bi_2O_3 additive which induced very homogeneous crystallization of the superconductor grains, with considerably controlled grain sizes, resulting, therefore, in a somewhat improved T_c, at 94 K, compared with 91 K for the sample prepared without additive [11].

The usual procedure to account for the variation in intensity of the diffraction peaks of $YBa_2Cu_3O_{7-\delta}$ is to correlate with the typical displacement phase transitions in perovskite structure [12]; however, for simplicity we ignore at present the specific displacements of ions in the unit cell which has a distorted orthorhombic layered perovskite structure. The ideal orthorhombic layered structure unit cell has the ratio for the axes $a = b = c/3$ and can be treated to comprise three substructures of cubic symmetry. In this approximation, most reflections present identical values of interplanar spacing, (d_{hkl}) and they comprise similar structure factors. For example, the reflections (0 0 6) and (0 2 0) have similar structure factors; $F_{006} = F_{020}$, and therefore their positions are not resolved in the diffractogram of an as-prepared $YBa_2Cu_3O_7$. Annealing at $T_a \sim 500\,°C$ or higher, modifies the lattice axes (and hence the d_{hkl} values) and so the two reflections are more clearly resolved.

As pointed out above, annealing of $YBa_2Cu_3O_7$ caused oxygen vacancies which may reside either along central-cage Cu–O chains replacing O(4) or O(5) ions, or substitute for O(1) ions along side chains

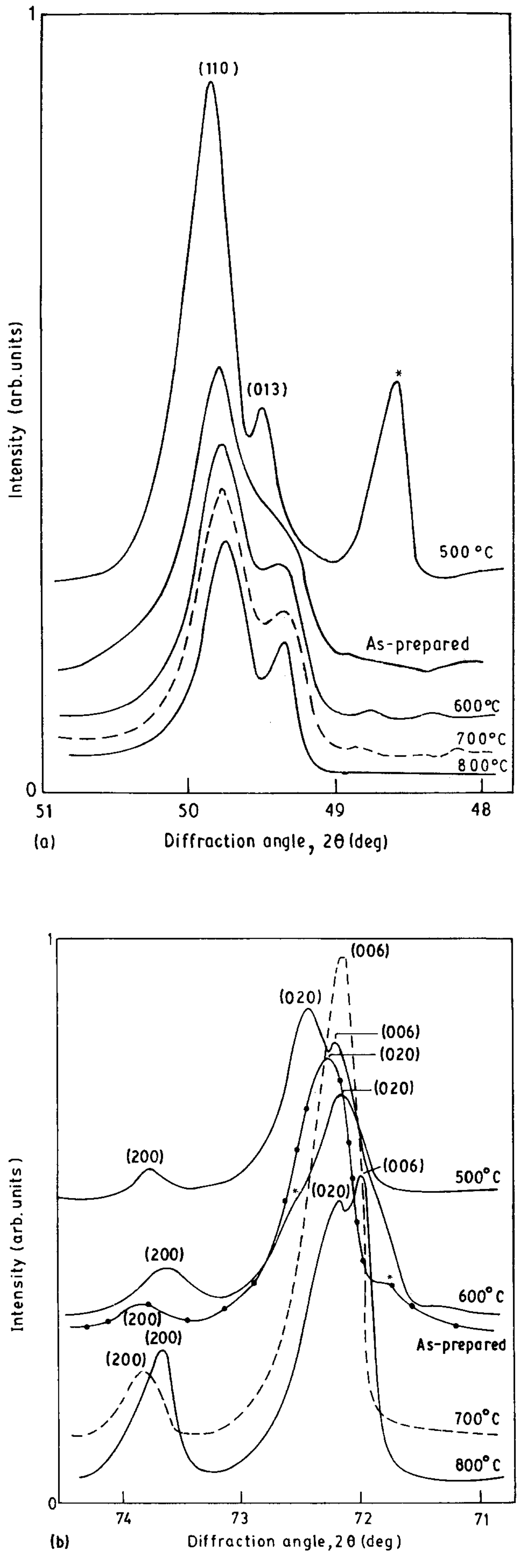

Figure 5 The effects of thermal annealing on $YBa_2Cu_3O_7$ showing the variations in peak positions, intensities and half-bandwidths for the characteristic diffraction peaks portrayed on a rather expanded 2θ scale: (a) 48°–51°, and (b) 70°–74°. The annealing temperatures are shown on the respective diffractograms. Peaks marked (*) are not firmly assigned.

TABLE I Crystal lattice parameters, oxygen content, δ, and T_c for $YBa_2Cu_3O_{7-\delta}$ superconductors annealed at several temperatures under a reduced air pressure of ~ 10 mbar

Annealing conditions		Lattice parameters (nm)			T_c (K)	δ (% molecule^{-1})
T_a (°C)	Time (min)	*a*	*b*	*c*		
As-prepared sample	–	0.3810	0.3884	1.1652	91	0
500	30	0.3812	0.3877	1.1658	89	0.31
600	30	0.3821	0.3888	1.1615	50	0.34
700	10	0.3811	0.3880	1.1661	70	0.45
800	20	0.3819	0.3887	1.1682	semicond.	0.76

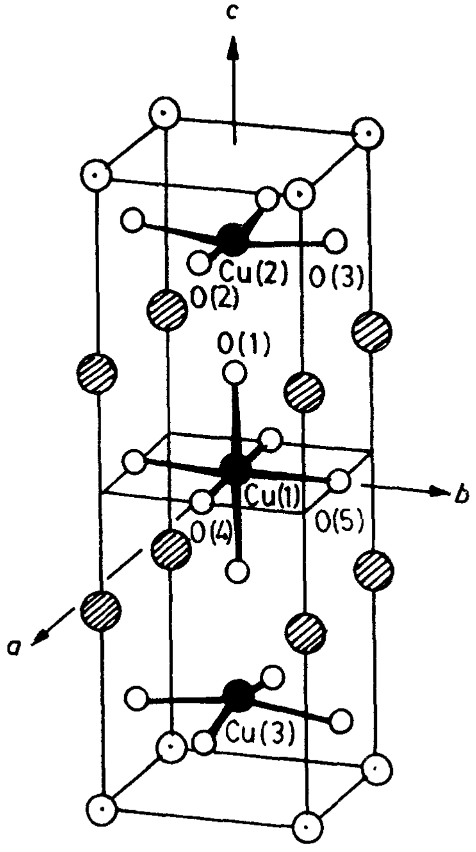

Figure 6 Orthorhombic crystal unit cell structure of $YBa_2Cu_3O_{7-\delta}$ showing the positions of the different (●) copper and (○) oxygen sites.

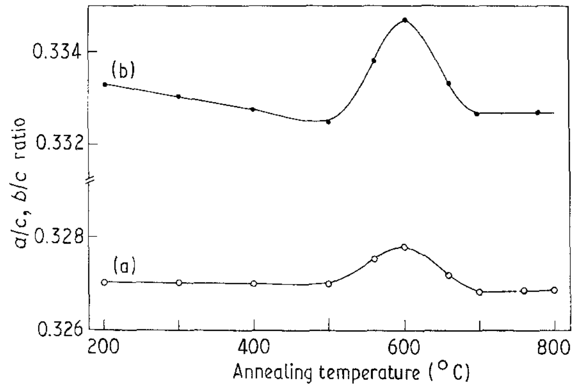

Figure 7 Variation in axial ratios (a) *a*/*c* and (b) *b*/*c* for the orthorhombic crystal unit cell of $YBa_2Cu_3O_7$ on annealing at different temperatures.

(cf. Fig. 6). The former break up spinal Cu–O linkages and oxygen sites no longer present parallel layered structures which are crucial for the high T_c temperature. Our annealed samples (except that annealed at 700 °C), suffer as expected, with the high T_c superconductivity properties, and coincidently present smaller values for the *c*-axis because of the shortening of the distance between the different copper sites. The values of the *a*, *b* and *c* crystal (orthorhombic) axes and the T_c for $YBa_2Cu_3O_{7-\delta}$, annealed at different T_a (500–800 °C), are given in Table I. Despite the fact that several processes take place in a complicated manner during annealing, the ratio (aspect) for the axes *a*/*c* or *b*/*c* follows a systematic trend with varying T_a, showing a peak for T_a around 600 °C in the *a*/*c* or *b*/*c* versus T_a plots, Fig. 7. In addition, the isothermal annealing of the sample at the 600 °C influenced T_c (which decreased from 91 K to 50 K) a maximum. A deviation of the aspect ratio, in particular, for *b*/*c* from an ideal value of 1/3 thus seems to be an important factor in the deterioration of the high T_c superconductivity properties during annealing.

Annealing, peculiarly, at a higher $T_a = 700$ °C, probably also removes the oxygen from O(1) sites which become positively charged on trapping holes, and thus enhance the superconductivity properties, because the carriers in $YBa_2Cu_3O_{7-\delta}$ superconductors are identified to be holes [13]. A pairing between these holes can be considered through the mediation of the oxygen vacancies [14, 15], which possibly favours the oxygen layered structure of the unit cell, in agreement with the prominent intensity of the (0 0 6) diffraction peak, which represents the reflection from the plane parallel to the oxygen layers, observed in the sample annealed at ~ 700 °C for 10 min (Fig. 5b). The layered oxygen configuration structure of the unit cell which, in fact, is kinetically governed by the oxygen vacancies around the copper sites, is thus crucial for high T_c superconductivity properties in $YBa_2Cu_3O_{7-\delta}$. A redistribution of the oxygen vacancies among the favourable sites does occur during annealing, optimizing the volume and energy of the system at the scale of the unit cell. As a result, the $YB_2Cu_3O_7$ annealed at 700 °C, for a short period of 10 min, though comprising an effectively smaller oxygen content (δ ~ 0.5), gives rise to a crystal unit cell volume of about the same value (cf. the lattice parameters in Table I) and exhibits, as expected, small electrical resistivity, with T_c at ~ 70 K, as for samples without annealing. The superconducting transition temperatures, T_c, of ceramic $YBa_2Cu_3O_{7-\delta}$ samples as a function of δ have been studied by many other authors (see, for example, [5]). In all other reports, the typical T_c for δ ~ 0.5 is reported to be below 50 K. We also noticed that our sample (annealed at 700 °C) slowly absorbs oxygen even at room temperature, producing an inhomogeneous oxygen distribution in the sample, when left in air for long period, and that, of course, presents considerably enhanced electrical resistivity signals with the T_c appearing at consistently much lower temperatures.

4. Conclusions

Thermal annealing of $YBa_2Cu_3O_7$, effectively at temperatures (T_a) between 400 and 800 °C, under a reduced air pressure of ~ 10 mbar, causes the oxygen interstitial vacancies in the crystal (orthorhombic) lattice, which reside prominently along the central Cu–O chains replacing O(4) ions or substituting for O(1) sites along the side chains. The results suggest that the oxygen vacancies initially populate O(4) sites, for $T_a \leqslant 600$ °C, and thereby break the spinal Cu–O linkages (which are crucial for the high T_c), resulting in a deterioration of the high T_c superconductivity properties. However, peculiarly, annealing at a higher $T_a \sim 700$ °C, for a short period of 10 min, also populates the oxygen vacancies on O(1) sites which become positively charged, being trapped on holes, and contribute to the superconduction process, so that the high T_c superconductivity properties do not suffer so much. The present results support the "hole pairing" model, recently suggested by Georgiev and Borissov [15], for the high T_c superconductors where the holes are the dominant charge carriers.

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