# Influence of preparation conditions on characteristics of the $YBa_2Cu_3O_{7-\delta}$ compound

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Synthesis of ceramic $YBa_2Cu_3O_{7-\delta}$ by solid-state reaction was performed under different conditions. Different values of cooling rate and oxygen flow were used, and no significant influence on superconducting characteristics of the samples was observed. A major influence on their mechanical properties was found.

## 1. Introduction

Since the discovery of superconductivity in ceramic compounds [1], many authors have reported the preparation of these materials under a wide variety of conditions [2–4], chosen according to the experience of each author [5]. However, there are only a few systematic reports about the influence of these conditions on structure, critical temperature, $T_c$, etc. [6–12].

Among almost 50 different rare-earth based compounds, the $YBa_2Cu_3O_{7-\delta}$ superconductor is the most studied so far. For example, it is well known that it presents a non-superconducting tetragonal phase, and it is necessary to make a transition to an orthorhombic structure to obtain the superconducting phase. This is done by a thermal treatment, and by an oxygenation process of the sample, either in air or in flowing oxygen.

In this work, we prepared samples of the superconductor $YBa_2Cu_3O_{7-\delta}$ under different oxygen flows and cooling rates in a range that has not yet been reported, as far as we know. Electrical resistance, hardness and density of these samples were measured; oxygen content was determined by thermogravimetric analysis (TGA) and structure was determined by X-ray diffraction.

## 2. Experimental procedure

The samples were prepared by the solid-state reaction method. A dense, sintered pellet of the superconducting compound was prepared by mixing powders of CuO, $Y_2O_3$ and $BaCO_3$. This pellet (13.25 mm diameter, 1.55 mm thick) was pressed at ~ 20 000 p.s.i. ($10^3$ p.s.i. = 6.89 nl $mm^{-2}$), annealed at 900 °C for 24 h, calcined at 950 °C for 4 h, then cooled to 400 °C at different rates, oxygenated in air or flowing oxygen for 2 h, and finally quenched to room temperature. The 950–400 °C cooling rates used were 25, 50 and 100 °C $h^{-1}$. Also, one sample was quenched (rate ~ 750 °C $h^{-1}$). The flow of oxygen was varied, taking the values 60, 80 and 100 l $h^{-1}$. Other authors have used flows as low as 0.6 l $h^{-1}$ [13], or as high as 60 l $h^{-1}$ [8]. In this work, we intended to extend the range.

The resistivity of the samples was measured by the four-probe method. Oxygen content was determined by TGA measurements in an equipment Perkin–Elmer Model TGS-2. X-ray diffraction analyses were performed in a Debye–Scherrer camera, lattice parameters were determined by a least-square fitting. Brinell hardness was measured in a hardness tester (107930, Galileo), and density was obtained by weighing the sample and dividing by its apparent volume. An analytical balance was used, with an accuracy of $10^{-1}$ mg.

## 3. Results and discussion

All 16 samples presented a resistance drop to zero when they were cooled. Fig. 1 shows the resistance–temperature plot of the sample with the highest $T_0(R = 0)$, i.e. $T_0 = 94$ K. This sample also has one of the sharpest transitions ($T_{onset} - T_0 = 8$ K), and has the lowest value of $R_0$ (resistance at 273 K). This sample was prepared under an oxygen flow of 80 l $h^{-1}$ and quenched. This suggests that a very low cooling rate is not necessarily the best way to prepare a good ceramic superconductor. However, it is interesting to note that the sample having the "worst" properties: $T_0 = 86$ K, $T_{onset} - T_0 = 20$ K, and $R_0 = 7.37$ mΩ, was also quenched, but now it was oxygenated in air.

Table I gives the results of Brinell hardness, oxygen content and density of the samples as a function of oxygen flow and cooling rate. An oxygen flow of

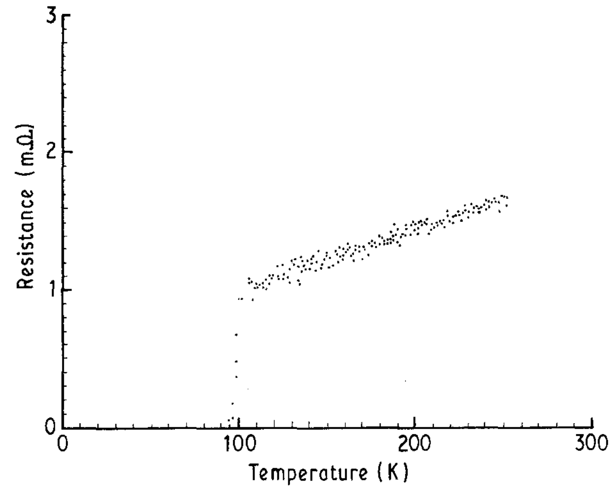


*Figure 1* Resistance as a function of temperature for the sample quenched and oxygenated at $80\,l\,h^{-1}$. This sample exhibited the highest $T_0$ (zero resistance): 94 K.

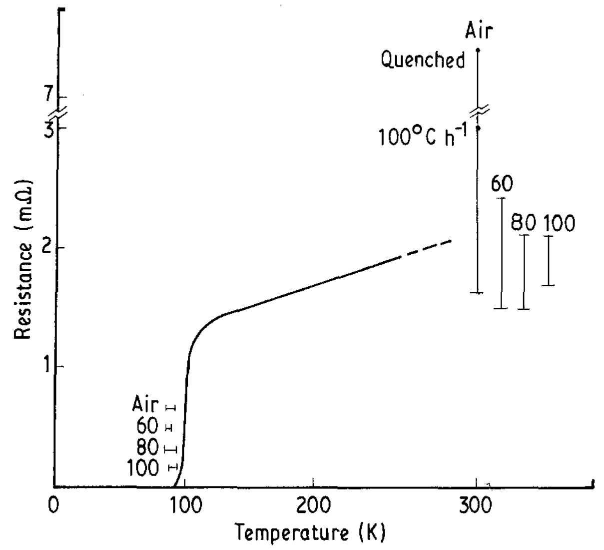


*Figure 2* Representation of $\delta R_0$ (vertical bars) and $\delta T_0$ (horizontal bars) for samples prepared under different oxygenation conditions: in air, and under 60, 80 and $100\,l\,h^{-1}$ oxygen flows. Resistance–temperature curves for all samples fall within these ranges (a typical curve is drawn). Note the relatively high value of $R_0$ for the sample quenched and oxygenated in air.

$0\,l\,h^{-1}$ indicates oxygenated in air, and the $750\,°C\,h^{-1}$ figure represents the quenched treatment. Variations in oxygen content and density were not significant; we could not observe any systematic behaviour or relation to the preparation conditions. However, it can be noted that the Brinell hardness of the samples prepared at high cooling rates ($100\,°C\,h^{-1}$ or quenched) was lower than the others; these samples had the common feature that they were very loose; in fact, five of these samples cracked and crumbled during measurement.

The resistance drop was observed to be quite similar for all samples. $R_0$ ranged between 1.5 and 7.37 mΩ, and $T_0$ lay in the interval 78–94 K. Fig. 2 shows a schematic plot of the ranges of $R_0$ ($\delta R_0$) and $T_0$ ($\delta T_0$) for samples prepared under different oxygenation conditions. It is clear that, as the flow is increased, $\delta R_0$ decreases; but no systematic influence on $\delta T_0$ was seen.

TABLE I Characteristics of $YBa_2Cu_3O_{7-\delta}$ as a function of cooling rate and oxygen flow

| Cool. rate ($°C\,h^{-1}$) | Oxygen flow ($l\,h^{-1}$) | $T_c$ (mid-point) (K) | Brinell hardness | Oxygen content ($7-\delta$) | Density ($g\,cm^{-3}$) |
|---|---|---|---|---|---|
| 25 | 0 | 96 | 140 | 6.7 | 4.5 |
| 25 | 60 | 96 | 150 | 6.71 | 4.9 |
| 25 | 80 | 97 | [a] | 7.01 | 4.4 |
| 25 | 100 | 98 | 120 | 6.79 | 4.7 |
| Mean values | | 96.8 | | 6.80 | 4.6 |
| σ | | 0.8 | | 0.12 | 0.2 |
| 50 | 0 | 93 | 140 | 7.14 | 5.0 |
| 50 | 60 | 90 | 170 | 6.88 | 5.0 |
| 50 | 80 | 94 | 180 | 7.12 | 4.7 |
| 50 | 100 | 94 | [b] | [b] | 4.4 |
| Mean values | | 92.8 | | 7.05 | 4.8 |
| σ | | 1.6 | | 0.12 | 0.2 |
| 100 | 0 | 96 | [a] | 6.53 | 4.4 |
| 100 | 60 | 97 | [a] | 7.02 | 4.7 |
| 100 | 80 | 93 | 100 | 6.78 | 4.6 |
| 100 | 100 | 84 | 100 | 6.65 | 5.0 |
| Mean values | | 92.5 | | 6.75 | 4.7 |
| σ | | 5.1 | | 0.18 | 0.1 |
| ≈ 750 | 0 | 92 | [a] | 6.85 | 4.7 |
| 750 | 60 | 91 | [a] | 6.75 | 4.4 |
| 750 | 80 | 98 | 110 | 7.03 | 4.9 |
| 750 | 100 | 98 | [a] | 7.19 | 4.8 |
| Mean values | | 94.8 | | 6.96 | 4.7 |
| σ | | 3.3 | | 0.17 | 0.2 |

[a] Crumbled while measuring.
[b] Not analysed.

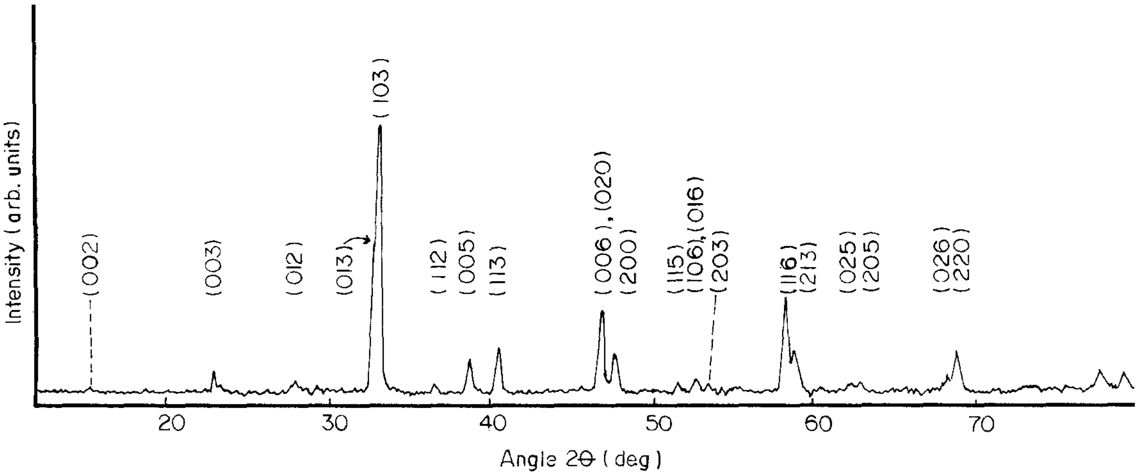


*Figure 3* XRD pattern of a sample quenched and oxygenated at $80\,\mathrm{l\,h^{-1}}$. The orthorhombic structure is well defined, and virtually no extra lines were observed. All samples had very similar spectra.

This only allows us to conclude that we have a good reproducibility of the superconducting transition to zero resistance of the samples. Only two samples, those prepared at the highest cooling rates and oxygenated in air, had slightly higher $R_0$. This increase of $R_0$ for samples oxygenated in air has been observed before [6, 14].

X-ray data show that all samples were orthorhombic. Fig. 3 shows a typical spectrum; almost no extra lines are observed, and it can be concluded that the samples were very pure. There were no significant differences in their lattice parameters, which were similar to the values commonly reported [4] ($a = 0.382 \pm 0.001$ nm, $b = 0.388 \pm 0.001$ nm and $c = 1.167 \pm 0.002$ nm).

## 4. Conclusions

Ceramic samples of $YBa_2Cu_3O_{7-\delta}$ were prepared under different cooling rates (25–750 °C $\mathrm{h^{-1}}$) and oxygenation conditions (in air, or under $60\text{–}100\,\mathrm{l\,h^{-1}}$ oxygen flow); all 16 samples were superconducting and, within accuracy and reproducibility of our measurements, some trends were observed and the following conclusions can be drawn.

1. The samples prepared at high cooling rates and oxygenated in air had slightly higher room-temperature resistance than those samples prepared at a lower cooling rate and oxygenated in an oxygen atmosphere. The reproducibility of resistance of the samples as a function of temperature was improved as the oxygen flow increased.

2. These two preparation conditions had no significant influence, within the ranges used in this work, on structure, lattice parameters, oxygen content and density of the samples; rather they determine their hardness. In this sense, the quenched and 100 °C $\mathrm{h^{-1}}$ cooled samples were of poor quality because they resulted in very loose samples.


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