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Influence of grain size and stoichiometry on the electrical behaviour of YBa$_2$Cu$_3$O$_{7-\delta}$

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Résumé. — Cette étude est relative au rôle de la microstructure sur les propriétés électriques de YBa$_2$Cu$_3$O$_{7-\delta}$ polycristallin. Les données expérimentales concernent les effets de la variation de taille de grains, d'une part, et l'écart à la stœchiométrie, d'autre part, sur la densité de courant critique à champ nul, mesurée à 77 K, et la résistivité à température ambiante. Tout d'abord, une forte décroissance de la densité de courant critique est observée lorsque la taille moyenne des grains excède 15 μm. Les gros grains favorisent les microfissures liées aux changements anisotropes de volume pendant le refroidissement depuis la température de frittage. Ces microfissures réduisent la section efficace du matériau capable de transporter le courant. Les mesures par ultra-sons confirment qu'il existe une augmentation de la quantité de microfissures dans les échantillons possédant de gros grains. Par ailleurs, une modification importante des propriétés électriques est observée lorsque les écarts à la stœchiométrie sont supérieurs à 0,5 mol %. D'autres travaux ont montré que la présence de phases minoritaires conduisent à des courants critiques plus faibles. Un écart à la stœchiométrie dans la poudre de départ favorise la formation de phases minoritaires. En conséquence, le choix d'un procédé d'élaboration de la céramique doit prendre en compte ces paramètres.

Abstract. — The role of the microstructure for the electrical properties of polycrystalline YBa$_2$Cu$_3$O$_{7-\delta}$ is examined. Experimental data are presented showing the effect of (i) variation in grain size and (ii) deviation from stoichiometry for YBa$_2$Cu$_3$O$_{7-\delta}$ on the critical current density in « zero » field at 77 K and the room temperature resistivity. Firstly a strong decrease in the critical current density has been observed when an average grain size of 15 μm is exceeded. Large grains promote microcracks due to anisotropic volume changes during cooling from the sintering temperature. This causes a reduction in the effective current carrying cross-section of the material. Ultrasonic measurements were used to confirm an increase in the microcrack density for large grained samples. Secondly, a significant modification of the electrical properties was achieved for deviations from stoichiometry greater than 0.5 mole %. Previous work has shown that the presence of minor phases due to incomplete calcination or poor mixing leads to reduced critical current density. Deviations from stoichiometry of the initial powder will also promote minor phases. These two aspects must be taken into account in the choice of a suitable ceramic processing route.

ntroduction.

The electrical properties of ceramic superconductors in the YBa$_2$Cu$_3$O$_{7-\delta}$ family are strongly influenced by the microstructure relating to the method and details of preparation. For example thin films carry critical currents greater than 10^5 A.cm^{-2} [1] whereas bulk ceramics yield values typically in the range 10^2 – 10^3 A.cm^{-2}. These lower critical current densities in the bulk ceramics are generally explained by the presence of weak links separating superconducting regions.

Several types of defect in the microstructure may contribute weak link behaviour. The materials are in essence 2-dimensional conductors (or superconductors) and the mismatch of grains which will occur in a microstructure with random grain orientations decreases the critical current density, j_c [2]. TEM studies have shown the presence of structural defects such as intergrowths and twinning [3], suggesting another source of weak links at the scale of a few atomic distances. In addition, pores, microcracks, and insulating minor phases will also play a signifi-

cant role. These last three factors can be distinguished from true « weak links » since their most important effect is to reduce the effective current carrying cross-section which however also leads to a smaller critical current. The separation of the effects of the different imperfections in the ceramic microstructure is an intrigueing and technologically important problem.

In this perspective, the present paper examines the changes in the electrical properties of bulk ceramic $YBa_2Cu_3O_{7-\delta}$ which occur for (i) variation in grain size, and (ii) deviation from stoichiometry. A simple model to facilitate interpretation of the experimental data is also presented. Another important parameter is the oxygen content of the samples. McNalford et al. [4] have shown that j_c decreases for densities greater than 92 % of theoretical density which is explained by inhibited access of oxygen to the interior of the sample. The transformation from the tetragonal to the orthorhombic phase occurs during cooling from the sintering temperature and requires oxygen uptake. The samples in this study had densities in the range 85-90 % of the theoretical density permitting a satisfactory oxidation. The penalty of a reduced effective cross-section due to 10 % porosity should not be too severe [5].

Experimental.

1. PREPARATION. — Bulk ceramic samples were prepared using standard procedure. This involves grinding the stoichiometric mixture of Y_2O_3, CuO, and $BaCO_3$ powders by hand with mortar and pestle, calcination at 940 °C, and sintering of the pressed disc at 975 °C in air. The purity of the starting powders was 99.99 % or greater. X-ray diffraction measurements indicated minor quantities of CuO and $BaCuO_2$ in the calcined product. The firing cycle also includes an annealing step at 600 °C followed by slow cooling (1 °C/minute) down to room temperature. Some of the samples were reannealed in oxygen at approximately 500 °C to promote the tetragonal to orthorhombic transformation.

Another series of samples was obtained using a powder prepared by a dissolution-recrystallization route in an organic medium. The average crystallite size of the powder was determined by Sherrer's method and is of the order of 0.1 μm.

2. CHARACTERIZATION. — Densities of sintered material were evaluated using Archimedes' principle. The microstructure was examined by scanning electron microscopy and the average grain size was estimated with Jeffries procedure. For electrical characterization samples were cut and polished in the form of thin bars, typically 1.1 cm long with a cross sectional area of 0.01 to 0.02 cm². The room temperature resistivity and the current-voltage behaviour at 77 K in « zero » magnetic field were

measured using a 4-terminal configuration. « Zero » field refers to zero applied field but includes the presence of the earth's magnetic field of approximately 0.5×10^{-4} T. Electrical contact was achieved using silver epoxy paint which yielded an electrode resistance of less than 5 ohms reproducibly. Heating effects on the current carrying terminals were minimized by immersion of the sample in liquid nitrogen. The critical current density was evaluated using a criterion of 1 μV/cm between the voltage sensing electrodes.

Results and discussion.

1. POLYCRYSTALLINE ASPECTS IN THE ELECTRICAL BEHAVIOUR. — In common practice, the electrical behaviour of a ceramic superconductor is characterized by the critical current density at 77 K in « zero » field, j_c, and the normal state resistivity at room temperature, ρ_{300}. From a technological point of view the aim is to achieve the maximum possible value of j_c. This should be associated with a low value of ρ_{300} since the imperfections in the ceramic which limit j_c also yield additional resistance in the normal state. As an example, consider the introduction of a hypothetical crack into the ceramic such that the effective current carrying cross-section is reduced by a factor of 2. Earlier work has shown that the critical current is directly proportional to the sample cross-section [6] and hence the measured critical current density will be halved while the measured resistivity doubles. However microstructural changes can be envisaged where j_c and ρ_{300} are not so directly related.

(a) *Normal state.* — Studies of single crystals show that the resistivity in the a-b plane depends linearly on the temperature which can be attributed to scattering of charge carriers by phonons [7-9]. Similar behaviour is observed for polycrystalline material [9], suggesting that the resistance to charge transfer at the grain boundaries does not influence significantly the overall character of the response in the ceramic and the dominant contribution is due to the bulk of the grains (otherwise, if the grain boundaries presented large barriers to charge transfer compared to the grains an Arrhenius type behaviour would be obtained as in, for example, zinc oxide varistors at low applied voltages). However values of ρ_{300} generally situate in the range 0.9-1.0 mΩ-cm for the best bulk ceramics compared to 0.15 mΩ-cm for a single crystal (a-b plane). The discrepancy can be explained by voidage, grain misalignment, and possibly minor phases which reduce the effective current carrying cross-section without crossing a percolation threshold such that there is a change in the character of the electrical behaviour as a function of temperature. A simplified schematic and equivalent circuit is given in figure 1a.
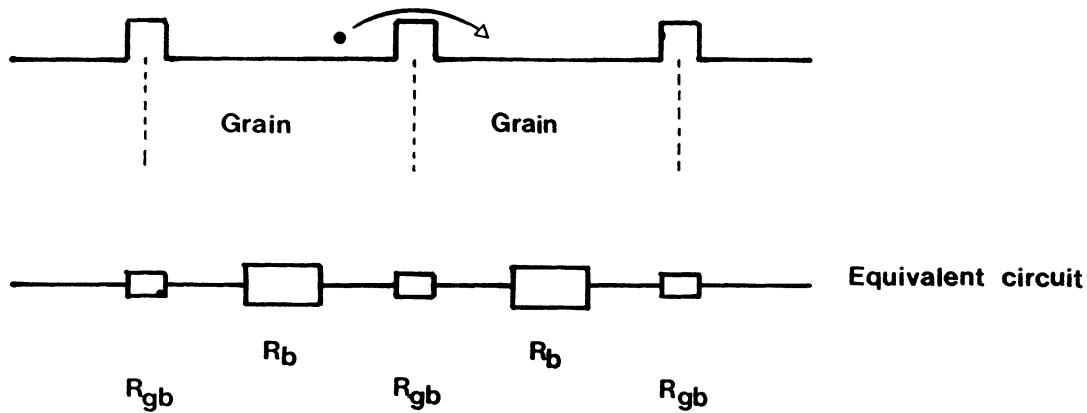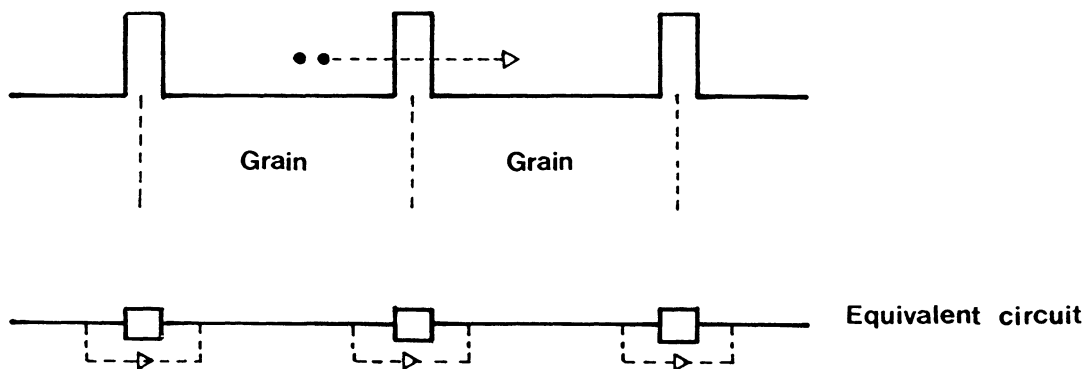
[a] Normal State

[b] Superconducting State

Fig. 1. — Idealized schematic of the electrical response for polycrystalline $YBa_2Cu_3O_{7-\delta}$.

(b) *Superconducting state*. — At 77 K the grains in polycrystalline material, in a first approximation, have zero resistance. But the grain boundaries which previously gave neglible resistance to charge transfer, now become significant barriers and dominate the electrical response by acting as weak links, figure 1b.

Consequently, any alterations to these barriers should have a pronounced effect on j_c without necessarily modifying ρ_{300} very much. In contrast, microstructural changes such as an increase in porosi-
effective current carrying cross-section should be revealed by both j_c and ρ_{300}.

2. GRAIN SIZE. — Two schools of thought exist concerning the effect of grain size on j_c. The first considers that a reduction in the number of grain boundaries (hence large grains) leads to an increase in j_c [10]. Alternatively Chiang *et al.* [11] have concluded from their experimental data on $La_{2-x}Sr_xCuO_4$ that only the weakest link determines j_c and that grain size has little role. In addition to this

aspect the effect of grain size for microcracking must be taken into account.

Previous work showed that the microstructure evolves as a function of sintering time by (i) grain growth, and (ii) change of grain shape from long thin rectangular shaped grains to a more rounded and equiaxed form [6]. These changes can be explained by the involvement of a liquid phase during sintering due to the presence of residual CuO after the calcination step.

Samples were sintered for different durations in or er o s u y e e ect o grain growt on t e electrical properties. The density, grain size, and room temperature resistivity ρ_{300} measurements are summarized in table I. For sintering times of 20 hours and longer the density of the samples is constant within error and therefore this factor should not influence the data significantly. Reannealing the samples in oxygen leads to higher values of j_c due to an increase in oxygen content, figure 1. For both air annealed and oxygen reannealed samples the increase of grain size has little apparent effect on j_c and ρ_{300} for sintering times up to 45 hours. If any

trends exist they can be explained by a slight increase in density between 10 hours and 20 hours sintering or they are obscured by the scatter of the data. However samples which are sintered for 60 hours exhibit a pronounced drop in j_c with a parallel increase in ρ_{300}. Furthermore the air annealed and oxygen reannealed samples have similar values of j_c suggesting the oxygen content is no longer different between the two sets of samples.

Table I. — *Density, grain size, and room temperature resistivity measurements for* $YBa_2Cu_3O_{7-\delta}$ *sintered at* 975 °C *with different durations.*

Sintering time (hours)	% of theoretical density	Grain size (μm)	Resistivity at 300 K (mΩ.cm) Air (*)	O₂ (**)
—	—	—	—	—
10	86	7	1.0	0.9
20	90	8	1.0	0.9
30	90	11	0.9	0.8
45	90	13	0.8	0.9
60	90	15	1.3	1.3-4.8

(*) annealed in air.
(**) reannealed in oxygen.

The simplest explanation is that microcracking has occurred. This yields a geometrical change on the microscopic scale in the sample such that there is a reduction in the effective current carrying cross-section. The presence of microcracks would also facilitate the movement of oxygen through the ceramic during annealing. Consequently reannealing in oxygen no longer increases the oxygen content.

In order to confirm this hypothesis ultrasonic non destructive tests were made on samples (discs, 10 mm in diameter and 3 mm thick) sintered for the same durations. The velocities v_L, v_T, and the attenuations α_L, α_T of 10 MHz longitudinal and transverse ultrasonic waves were measured using a pulse-echo technique. For a microcracked ceramic a decrease in v_L and v_T due to the deterioration of the elastic properties and an increase in α_L, α_T due to multiple scattering are expected as discussed elsewhere [12]. The results show such effects as a function of sintering time, figure 2. Though the sample density is greater for longer sintering times which should lead to higher ultrasonic velocities, a decrease is observed for both v_L and v_T. Furthermore, whereas samples sintered for 20 hours did not exhibit any propagation difficulties, there was such an increase in attenuation for longer sintering times that no echo was observed for longitudinal waves in 45 and 60 hour samples, and similarly for transverse waves in 30, 45, and 60 hour samples. Figure 3
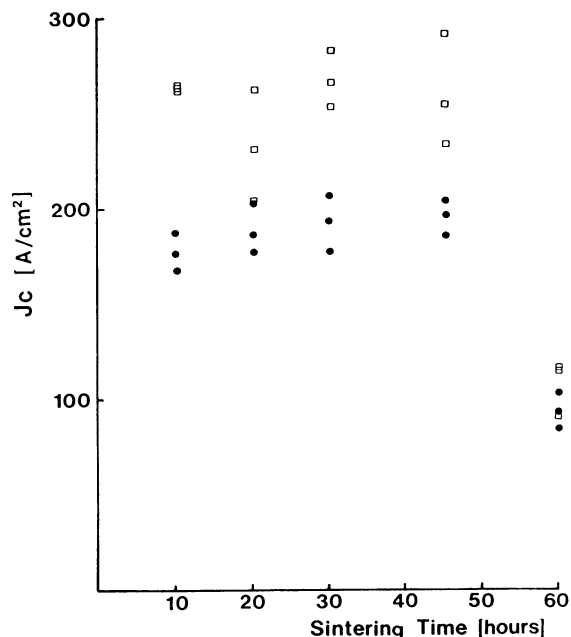

Fig. 2. — Critical current density measured at 77 K in « zero » field *versus* sintering time of polycrystalline $YBa_2Cu_3O_{7-\delta}$. The dots (•) represent samples which have been annealed in air. The squares (□) represent samples which have been reannealed in oxygen at 500 °C.
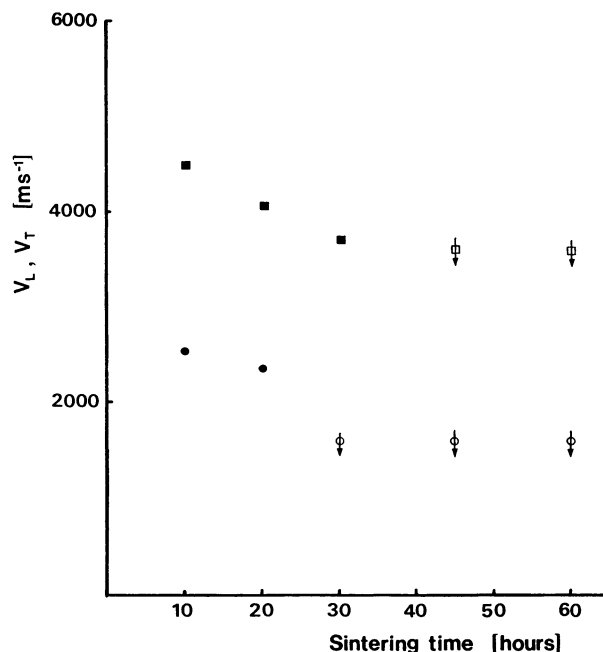

Fig. 3. — The velocities of longitudinal (squares) and transverse (dots) ultrasonic waves as a function of sintering time for oxygen reannealed polycrystalline $YBa_2Cu_3O_{7-\delta}$. The arrows indicate samples where the signal was too attenuated for measurement.

shows that in the extreme case of 60 hours sintering this microcracking occurs mainly along the grain boundaries.

The origin of these microcracks can be sought in terms of anisotropic volume changes of the grains during cooling from the sintering temperature giving rise to internal stresses. Such an effect due to anisotropic thermal expansion is well known in single phase polycrystalline ceramics and depends on the difference of thermal expansion coefficients along the crystal axes and on the grain size [13]. In this case the microcracks follow the grain boundaries as can be observed in figure 4. $YBa_2Cu_3O_{7-\delta}$ exhibits anisotropic thermal expansion but another source of microcracking may be significant due to oxygen uptake associated with the tetragonal to orthorhombic phase transformation. This is also accompanied by anisotropic lattice parameter changes. A change in the oxygen content at 500 °C from $7 - \delta = 6.37$ to $7 - \delta = 6.92$ yields $\Delta a = - 0.98 \%$, $\Delta b = + 0.49 \%$, and $\Delta c = - 0.53 \%$ [14].

The ultrasonic tests suggest that microcracking has even occurred for samples sintered for 10 hours and 20 hours. Calculation of Young's modulus gave
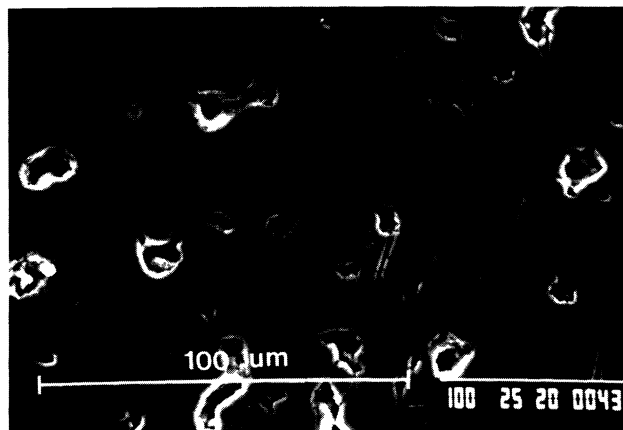
a)

b)

Fig. 4. — Micrographs of $YBa_2Cu_3O_{7-\delta}$ sintered for (a) 20 hours and (b) 60 hours.

values of 100 GPa and 85 GPa respectively. This can be compared to 130 GPa obtained by extrapolation of data by McN. Alford et al. [15] for a porosity of 10 %. Recent work by Shaw et al. [16] reports an onset of microcracking in polycrystalline $YBa_2Cu_3O_{7-\delta}$ for grain sizes of 1-2 μm. An important question is whether a number of microcracks can be tolerated in the ceramic before significant effect on the electrical response. It can be noted that a significant drop in j_c did not occur until a sintering time of 45 hours was exceeded. Alternatively an unidentified phenomenon may be masking the effect of the microcracks.

3. DEVIATION FROM STOICHIOMETRY. — Previous work has shown that the presence of minor phases due to incomplete calcination or poor mixing leads to reduced j_c [6]. Deviations from stoichiometry will also promote minor phases. We wished to explore (i) the level of stoichiometry which must be maintained before significant change in the electrical properties, and (ii) the effect on ρ_{300}.

In order to achieve an accurate control of the composition a chemically prepared powder was used. After sintering for 10 hours in air at 970 °C stochiometric $YBa_2Cu_3O_{7-\delta}$ yielded values of approximately 100 A.cm^{-2}. However microcracking

Table II. — Room temperature resistivity and critical current density at 77 K measurements for off stoichiometric compositions of $YBa_2Cu_3O_{7-\delta}$. The deviation is an excess in each case.

CuO deviation (mol %)	ρ_{300} (mΩ.cm)	j_c (A/cm^2)
0.2	2.0	101
0.5	2.9	77
1.0	4.1	63

BaO deviation (mol %)		
0.5	2.4	60
1.0	26.3	6

Y_2O_3 deviation (mol %)		
0.2	1.6	137
0.5	2.4	31
1.0	6.7	40

was thought to have occurred because large grains upto 80 μm long were observed by microscopy and reannealing in oxygen- did not result in a significant change in j_c. If the composition deviates by 0.5 % or greater j_c drops significantly in value, table II. Generally it is accompanied by a similar increase in ρ_{300}. This suggests that the minor phases which have been promoted are so insulating that their presence simply leads to a reduction in the effective current carrying cross-section. It can be noted that the sample containing 1 mole % excess Y_2O_3 exhibited widely dispersed spots of the green phase (Y_2BaCuO_5) visible to the naked eye.

Conclusions.

The role of the microstructure for the electrical properties of polycrystalline $YBa_2Cu_3O_{7-\delta}$ has been examined with respect to grain size, minor phases, and oxygen content. If a parameter participates in the control of the effective current carrying cross-section of the material then both j_c and ρ_{300} are influenced. Thus large grain sizes, which induce microcracks due to anisotropic volume changes on cooling from the sintering temperature, result in a decrease in j_c with a parallel increase of ρ_{300}. A significant increase in the microcrack density was confirmed by ultrasonic measurements for larger grained samples. An additional effect of microcracking is to facilitate movement of oxygen through the ceramic and hence the oxygen uptake which is associated with the tetragonal to orthorhombic phase transformation. The presence of minor phases due to deviation from stoichiometry (on a macroscopic or local scale) can also result in a reduction of the effective current carrying cross-section.

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