

Synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ at 1×10^5 Pa oxygen pressure

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Abstract

$\text{YBa}_2\text{Cu}_4\text{O}_8$ (124) powder has been synthesized by two different methods at 1×10^5 Pa oxygen pressure: (i) Solid state reaction of fine powdered $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (123) and copper oxide; (ii) A procedure using precursors of variable particle size in the μm range and uniform particle shape. The preparation of the stoichiometric precursor mixtures is carried out by a thermal decomposition of triethylene glycol complexes of yttrium, barium and copper in solution. The correlation between preparation conditions, microstructure and physical properties of such synthesized samples is discussed. Starting from the $\text{YBa}_2\text{Cu}_4\text{O}_8$ material, the influence of fine dispersed CuO within the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grains which are formed as a result of the thermal conversion of $\text{YBa}_2\text{Cu}_4\text{O}_8$ according to $\text{YBa}_2\text{Cu}_4\text{O}_8 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} + \text{CuO}$ ($T > 880^\circ\text{C}$) on the critical current density $J_{c, \text{mag}}$ (intragrain) of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is investigated.

1. Introduction

In addition to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (123-phase) the system Y–Ba–Cu–O contains two further superconducting phases: $\text{YBa}_2\text{Cu}_4\text{O}_8$ (124) with a T_c of 75–80 K (Ca-substitution leads to a T_c of 90 K [1]), and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ (247) with a T_c between 40–82 K [2].

Studies of the phase diagram [3, 4] prove that the $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor is a stable phase at 1×10^5 Pa O_2 and temperatures up to 850°C . At higher temperatures, $\text{YBa}_2\text{Cu}_4\text{O}_8$ becomes unstable and decomposes into $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15} + \text{CuO}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} + \text{CuO}$, respectively.

In contrast to the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ phase, the oxygen stoichiometry of $\text{YBa}_2\text{Cu}_4\text{O}_8$ remains constant up to 850°C and bulk samples quenched from high temperatures are still superconducting. This behaviour of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase might become of industrial interest.

Bulk $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor has been synthesized previously using a high-pressure oxygen technique (> 100 bar) [5]. However, it can be prepared at 1×10^5 Pa oxygen pressure starting from the hydrated nitrates in the presence of alkaline carbonate [7], using a precursor mixture of Y_2O_3 , BaCuO_2 and CuO [8] or on the base of a sol-gel technique [6, 9].

In this paper we report the preparation of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase by the solid state reaction using different starting materials at 1×10^5 Pa oxygen pressure. In addition, we have investigated the effect of the decomposition reaction $\text{YBa}_2\text{Cu}_4\text{O}_8 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} + \text{CuO}$ in view of a possible flux-pinning enhancement

in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grains.

2. Experiments

The $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase was synthesized starting from a stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder which was mixed with the appropriate amount of CuO powder (particle size $< 1 \mu\text{m}$). The mixture was ground, pressed into pellets, sintered at $810^\circ\text{C} - 830^\circ\text{C}$ for 24–48 hours at 1×10^5 Pa of flowing oxygen. Regrinding and firing were repeated 2–3 times and the final sintering was carried out at $T = 820 - 830^\circ\text{C}$ up to 10 days in flowing oxygen.

The $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase was also prepared using fine powder precursors. The technique of intramolecular thermal reduction in organic solution, which was used to prepare fine copper powders with controlled particle shape and size [10], has been modified for the synthesis of superconducting oxide ceramic precursors. Yttrium acetate, barium hydroxide and copper acetate, respectively, were treated with a large excess of triethylene glycol as a complexing agent. The obtained solutions containing the triethylene glycol complexes of yttrium, barium and copper were mixed and decomposed at enhanced temperatures. A systematic study was done in order to determine the optimum processing conditions resulting in the desired particle morphology and the right composition. The variables in this study were the concentration of reactants (i.e. $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and triethylene glycol), stirring

rate, heating regime and reaction temperature. Spherical particles ($\leq 1 \mu\text{m}$) of XRD-pure material with a ratio 1:2:4 were obtained by reacting a solution containing 0,0275 M $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, 0,0585 M $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and 0,105 M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in triethylene glycol at 270°C for 60 minutes and a heating rate of 8 K/min (Figure 1). An excess of Y and Ba in the solution is required to obtain the precipitate with stoichiometric 1:2:4 composition. The reaction product was hot filtered, washed with acetone and dried 5 h at 110°C . The precursor was heated at 400°C for 20 h in an oxygen atmosphere. Then, the material was pressed into pellets, sintered at 820°C for 48 h at $1 \cdot 10^5$ Pa of flowing oxygen.

The decomposition of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase was carried out by rapid heating up the sintered precursor sample (single phase $\text{YBa}_2\text{Cu}_4\text{O}_8$) and holding it at $890\text{--}920^\circ\text{C}$ for a short time (90–180 seconds) and final annealing at $T = 380^\circ\text{C}$ in flowing oxygen.

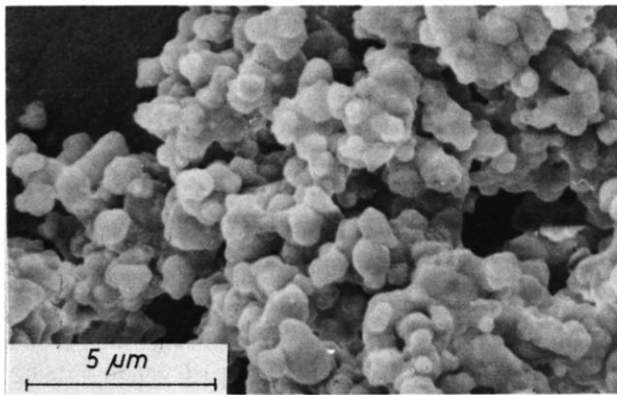


Figure 1. Scanning electron micrograph of precursor mixture

3. Results and discussion

The $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase was obtained with both different starting materials. In both cases, XRD indicated single phase powders. Independent of the preparation method, the AC susceptibility vs. temperature curves show a sharp transition into the superconducting state at 78 K (Figure 2). In Figure 3, the microstructure of the differently prepared $\text{YBa}_2\text{Cu}_4\text{O}_8$ powders have been compared on the base of optical micrographs of polished cross sections. Whereas the powder synthesized by solid state reaction of $123 + \text{CuO}$ leads to a relatively broad grain size distribution with an average value of about $10 \mu\text{m}$, the grains obtained with a precursor material are significantly smaller and the average particle size before and after the sintering process is in the magnitude of $1 \mu\text{m}$. Both samples indicate a few CuO particles (white areas).

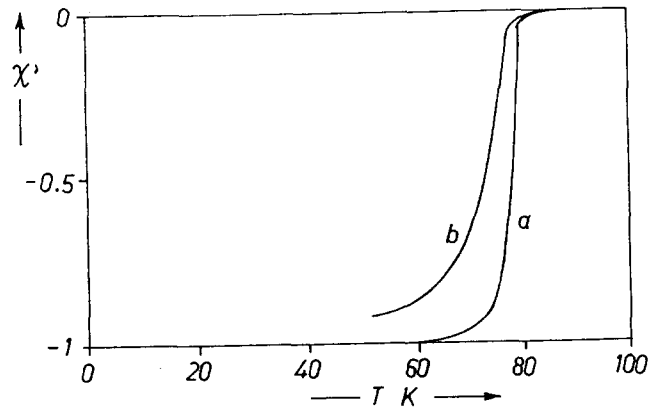


Figure 2. AC susceptibility vs. temperature curve of a $\text{YBa}_2\text{Cu}_4\text{O}_8$ single phase sample; (a) $H = 1 \cdot 10^{-5}$ T; (b) $H = 3 \cdot 10^{-4}$ T

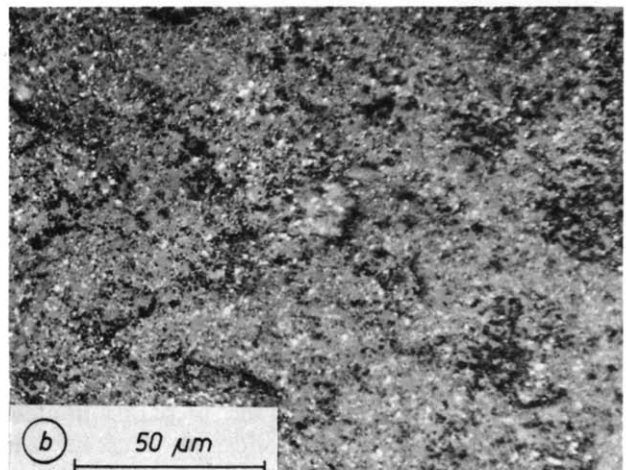
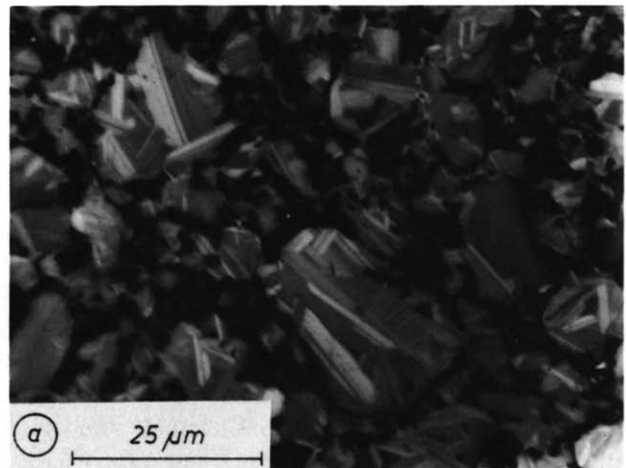


Figure 3. Optical microscopy pattern of polished cross section $\text{YBa}_2\text{Cu}_4\text{O}_8$ sample; starting materials: (a) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} + \text{CuO}$; (b) fine powder precursor

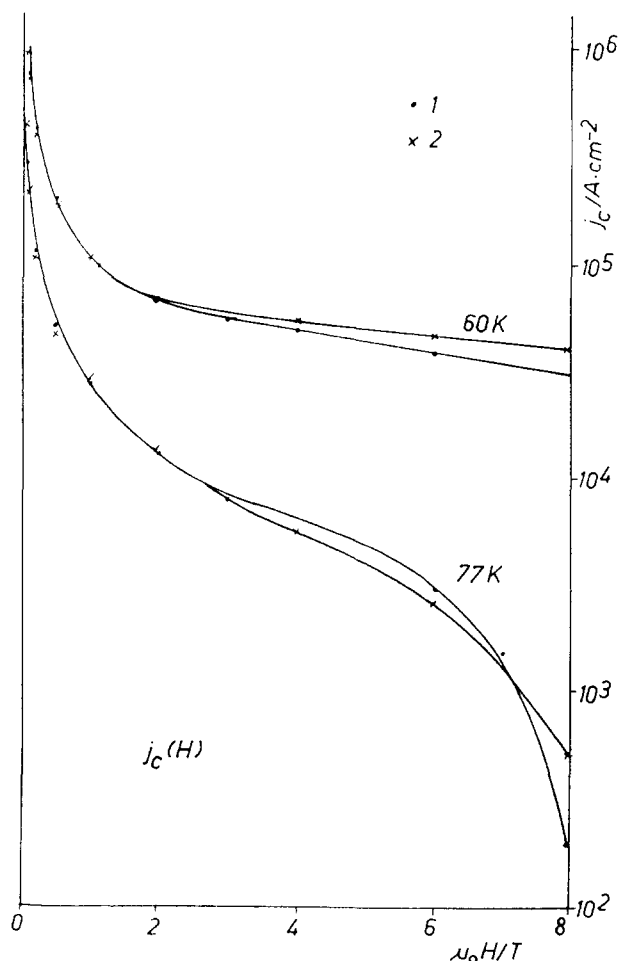


Figure 4. $J_{c, mag}$ as function of magnetic field of a samples consisting of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} + \text{CuO}$

However, optical microscopy pattern of polished cross sections of samples prepared from 123+ CuO show that the grains consist of two types of domains (Figure 3a). According to EDX analysis, areas with copper deficiency ($3.4 < \text{Cu} < 4$) at constant Y:Ba = 1:2 ratio have been observed besides ranges with the stoichiometric 1:2:4 composition. Usually, both kinds of domains are separated by sharp boundaries. Although it has not yet been verified by XRD, this result implies that the Cu-deficient regions (bright areas in Figure 3a) are related to the 247 compound. Only recently, Kaldis et al. reported the copper nonstoichiometry in the 247 phase as a result of stacking faults [11].

First results of the thermal decomposition of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase prepared via solid state reaction show a quantitative conversion into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and CuO at 920°C and 90 seconds. Magnetization measurements of these samples have been performed. Using

the Bean model, the intragrain critical current densities $J_{c, mag}$ were determined for ceramic samples prepared by cold isostatic (2) and uniaxial (1) pressing. The results show (Figure 4) that $J_{c, mag}$ rapidly decreases with increasing magnetic field at 77 K. Despite of the relatively short reaction time of 90 seconds, the copper oxide particles which are formed as a result of the thermal conversion are relatively large compared to the coherence length. Therefore, no favourable situation for an efficient flux pinning can be established. Further studies are necessary to decide if improved decomposition conditions (particularly in the T-t regime) or the application of $\text{YBa}_2\text{Cu}_4\text{O}_8$ fine powder (via the precursor synthesis path) lead to finer-scaled CuO precipitates within the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grains.

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