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LETTER TO THE EDITOR

Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by citrate synthesis and pyrolysis

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Abstract. A recent preparation method by citrate synthesis in combination with pyrolysis has been applied to the new high- T_c superconductors. A step-by-step procedure is given to obtain the ultra-fine and homogeneous powder. X-ray diffraction analyses were performed to characterise the powder and to study the influence of the calcination temperature. Resistance measurements exhibit complete superconductivity at 91.2 K.

In general $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is prepared, starting from the oxides, by a number of solid state reactions with grinding in between [1]. Although good results are obtained, this method takes much time to get good quality single-phase powder, without impurities such as CuO , BaCuO_2 and Y_2BaCuO_5 . Extensive grinding increases the homogeneity of the material, but the minimum obtainable particle size of the starting oxides ($\sim 1 \mu\text{m}$) severely hampers the solid state reaction. A method that solves this problem is citrate synthesis. The powder obtained by such a preparation technique is ultra-fine and already has the correct stoichiometric values. Therefore this type of preparation is fast and also simple. After the pyrolysis only one calcination (including the solid state reaction) is needed.

In this paper we report on the preparation conditions of this citrate synthesis in combination with pyrolysis. X-ray diffraction analyses were performed on the powder, in order to get information about the purity of the powder and the role of the calcination temperature, and on sintered pellets. Resistance measurements on these pellets show an onset temperature of 93.5 K and complete superconductivity at 91.2 K.

We prepared the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with the citrate synthesis technique in combination with pyrolysis to attain a homogeneous and ultra-fine powder without impurities [2]. The following recipe holds for 0.1 mol $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The BaCO_3 (5 mol l^{-1} , 39.47 g) is dissolved in 60 ml nitric acid (65%) with 80 ml Q_2 -water (it is necessary to heat the $\text{Ba}(\text{NO}_3)_2$ solution). The Y_2O_3 (4 mol l^{-1} , 11.29 g) and CuO (5 mol l^{-1} , 23.86 g) are solved in 40 ml nitric acid (65%) each. The three

solutions are put together and citric acid (126 g) is added. Besides the metal-organic complexes, a precipitate of barium, $\text{Ba}_3(\text{C}_6\text{H}_5\text{O}_7)_2$, forms. During the neutralisation with ammonia (NH_4OH , 25% solution), all reactants disappear and the liquid becomes dark blue at a pH of 6.5–7.0. The pH value is of utmost importance, for hydroxides and base salts will appear if it becomes larger than seven.

The solution (pH = 6.8) is heated in equal proportions of 100 ml on a hot plate in an oversized Pyrex two-litre breaker. During the heating a viscous mass forms, followed by a large swelling due to the citric acid, and, finally, spontaneous combustion is initiated by the ammonium nitrate (NH_4NO_3). The risen powder fills the glass completely and the resultant foam consists of homogeneous flakes with particles sizes of 50 to 100 nm. It is important that during the dry-up, no precipitates form and none of the citrate components ignites separately. The liquid has to stay clear until the glow front arises.

After the pyrolysis it is necessary to calcinate the powder. This can be done in combination with the solid state reaction. Good results were obtained with a calcination temperature of 920°C over 10 h and then cooling at a rate of 50°C h^{-1} , both procedures taking place in an oxygen flow. Afterwards pellets were pressed and sintered in an oxygen flow at 920°C for 10 h and cooled down with 50°C h^{-1} . The density of the sintered pellets was 86% of the theoretical value.

Using micro-element analysis we found in general less than 0.2% C in calcinated powder made by this citrate synthesis technique.

In order to characterise the powder made by citrate

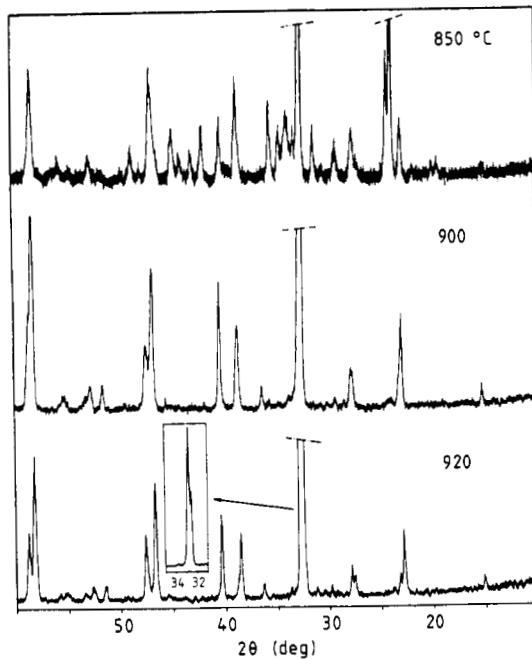


Figure 1. Powder x-ray diffraction patterns for powders produced at three calcination temperatures $T = 850\text{ }^{\circ}\text{C}$, $900\text{ }^{\circ}\text{C}$ and $920\text{ }^{\circ}\text{C}$.

synthesis, x-ray diffraction measurements were performed. We used a Debye-Scherrer diffractometer with $\text{Cu K}\alpha$ source. These investigations give insight into the occurrence of the correct orthorhombic crystal structure and the presence of impurities like CuO , BaCuO_2 and Y_2BaCuO_5 . The spectra of the powders obtained at three different calcination temperatures are given in figure 1.

The pattern of the powder, calcinated at $850\text{ }^{\circ}\text{C}$, already shows the main reflections of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Apart from this, reflections are recognisable from CuO ($2\theta = 35.55$ and 48.76 deg). The difference of calcination at $900\text{ }^{\circ}\text{C}$ is that the pure $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder gave x-ray reflections corresponding to a more tetragonal phase. The (hkl) reflections— (100) , (013) , (200) and (213) —are shifted with respect to the orthorhombic phase, indicating that the values of the lattice parameters a and b are levelling up. Clear reflections of impurities are not observed. Calcination at $920\text{ }^{\circ}\text{C}$ gives the expected x-ray pattern. The observed values of 2θ correspond with the orthorhombic lattice parameters $a = 3.82\text{ \AA}$, $b = 3.89\text{ \AA}$ and $c = 11.67\text{ \AA}$ [3].

It is worth mentioning that the $(0, 0, l)$ reflection intensities are larger in the sintered pellets than the corresponding values of the powder samples, indicating a preferential orientation of the c axis perpendicular to the surface. Again no impurities have been observed.

We performed resistivity measurements on sintered pellets by a four terminal AC technique as a function of temperature. The sample was placed in a copper housing together with a platinum resistance thermometer and cooled by a helium gas flow. Good electrical contacts were obtained by evaporating copper

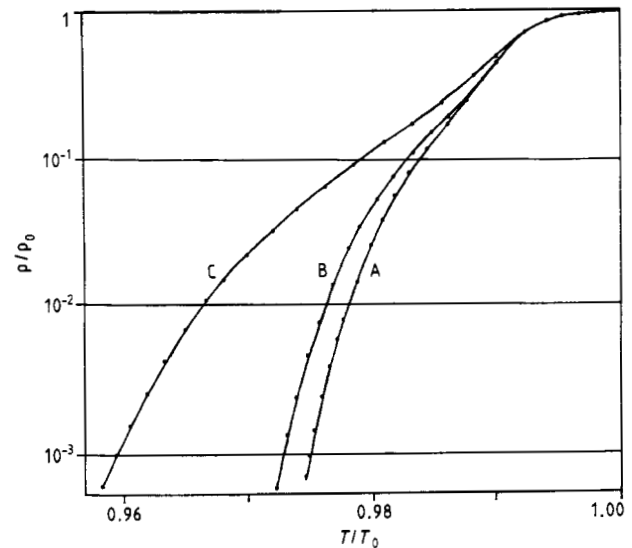


Figure 2. Relative specific resistivity versus temperature of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with a current density of; A, 2 A cm^{-2} ; B, 10 A cm^{-2} ; C, 40 A cm^{-2} . Parameters are $\rho_0 = 8.7 \times 10^{-6}\text{ }\Omega\text{ m}$ and $T_0 = 93.5\text{ K}$.

strips on which we soldered the contact wires. We varied the measuring current from 2 to 40 A cm^{-2} . In figure 2 the influence of the current density on the resistivity is presented. The onset temperature is $T_{\text{co}} = 93.5\text{ K}$ and is independent of the applied current. The specific resistivity (ρ_0) is $8.7 \times 10^{-6}\text{ }\Omega\text{ m}$ at $T = 93.5\text{ K}$, which is low compared to data from the literature. We relate this low value to the very good sample homogeneity obtained by our citrate and pyrolysis technique. The influence of the current density on the resistance gives information about the sintering process and is not a qualification of our powder preparation technology.

We succeeded in preparing an ultra-fine, homogeneous powder of the new high- T_c superconducting material. This powder appears to be useful for a number of applications. Besides its properties as a bulk material, it can be used with good results in a painting technique for the preparation of thick films. Also, targets for sputter deposition can be easily made.

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