Synthesis of YBCO superconductor by the method of combustion reaction in solution

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Abstract. Solutions of metallic nitrate were prepared to obtain the $Y_1Ba_2Cu_3O_{7−δ}$ and $Y_3Ba_2Cu_6O_{10−δ}$ phases in different mixtures of urea and glycine balanced stoichiometrically according to the principle of propellant chemistry to be synthesized by the method of combustion reaction in solution using a thermal blanket type furnace. The obtained powders required a post-reaction heat treatment at 920 °C for 2 h in air. The X-ray diffraction (XRD) characterization showed that the synthesized powders have a predominant superconducting $Y_1Ba_2Cu_3O_{7−δ}$ phase with an orthorhombic crystal structure and a complementary phase $Y_3Ba_2Cu_6O_{10−δ}$. The $Y_3Ba_2Cu_6O_{10−δ}$ phase was not found in any of the cases. The results of the transition electron microscopy (TEM) showed most grains with an average size of 300 nm and confirmed the Y123 phase. In addition, it was observed grains with an average diameter of 1.6 µm. The measurement of electrical transport gave a $T_c$ ~ 91 K by the 4-probe method and by SQUID magnetometry it was obtained a $T_c$ ~ 92 K for zero field cooled (ZFC) and field cooled (FC) magnetizations.

1. Introduction
Superconductor materials are applied for different purposes such as the production of very large magnetic fields and designing train prototypes based on magnetic levitation. Additionally, the latest investigations report a critical current density $J_c$ within the YBCO grains or film of about 1MAcm⁻² at 77 K. Moreover, the YBCO superconductor has an advantage over other superconductor based of Bi related to its applications in relation to its high critical current density $J_c$. Therefore, this advantage is suitable for applications in electrical industry.

The YBCO superconductor was synthesized for first time by C. Chu et al. [1] in 1987 by the solid state reaction method with transition temperature of $T_c$ ~ 92, however, this method has some disadvantages due to its long sample preparation procedure and a long synthesis time, around 16 h at 100 h in a procedure that it is repeated up to 3 times in a controlled atmosphere of oxygen. As a result, different methods have been proposed to obtain this superconductor in order to optimize the amount of material obtained or to simplify the procedures. Hence, Hsu et al. [2] in 1993 synthesized this material by spontaneous reaction requiring for the best obtained sample an heat treatment for 5 h at $P_{O_2} = 1$ atm with the aim of decreasing the additional phase as $Y_2Ba_1Cu_1O_5$ y BaCO₃ found. In 1997, Kato et al. [3] achieved to synthesize the pure phase of $Y_1Ba_2Cu_3O_{7−δ}$ using metal oxides by domestic microwave oven without post-heat treatment.
Although they managed to reduce the synthesis time to a few minutes, their method requires an laborious process of preparation of the sample previously.

Surprisingly in 2009, the last member of the YBCO family was discovered, which is also a superconductor. A. Aliabadi et al. [4] synthesized the superconductor \( Y_3Ba_2Cu_3O_{10-\delta} \) (Y358) by the traditional method of solid state reaction at 840°C for 12 h. The sample had a \( T_c \sim 102 \) K and the crystalline structure of this phase is very similar to the crystal structure Y123 with the exception of the number of CuO chains and CuO2 planes.

Since 2012, a new trend has been developed in using biopolymers to synthesize YBCO as Hall et al. [5] that successfully synthesized the \( Y_1Ba_2Cu_3O_7-\delta \) superconductor by the sol-gel method using biopolymers. Additionally, the advantage of using these biopolymers is due to the formation of texturized materials as nanowires. The powders obtained were dried for one day at 40°C and required a thermal treatment of 920°C in air for 2 h. The best obtained temperature \( T_c \) was 83 K with a critical current density \( J_c \) of 1.5 \( MAcm^{-2} \) at 10 K and 1 T of applied field. This critical current density exceeds the commercially available superconducting powders by almost 2 orders of magnitude (Aldrich 99.9%). After that Konne et al. [6] continued with this methodology to synthesize for the first time nanowires of the new superconducting phase Y358 obtaining \( T_c \) of 89.4 K that would naturally correspond to the Y123 phase. They justified the decrease in \( T_c \) is possibly due to morphology effects such as grain size or shape of the sample. Additionally, the critical current density \( J_c \) was 7.6 \( MAcm^{-2} \) at 10 K and 1 T of applied field.

In this letter, we report the synthesis of superconducting powders of \( Y_1Ba_2Cu_3O_7-\delta \) by the method of combustion in solution for first time using fuels: glycine and urea. The temperature \( T_i \) for the synthesis of the phase Y123 or Y358 have to be over to 800 °C [7] [6] and the previous experience in the synthesis in other compound of similar crystal structure [8] guarantees that mixture of the fuels achieves temperature above 800°C. The obtained powders needed a post-heat treatment at 920°C for 2 h. However, new phase Y358 have not observed in any of cases for this method.

2. Sample preparation and characterization

In order to synthesize the superconducting Y123 and Y358 powders, we have used the method of combustion in solution using nitrates as reactants, \( Y(NO_3)_3.6H_2O, Ba(NO_3)_2 \) and \( Cu(NO_3)_2.3H_2O \), and the fuels used in this synthesis were urea (U) and glycine (G). The nitrates and fuels were balanced weighted stoichiometrically according to the principle of propellant chemistry [9] to get 2 g of compound YBCO with a molar ratio of Y:Ba:Cu::1:2:3 and Y:Ba:Cu::3:5:8.

Additionally, other syntheses were made by varying the urea-glycine molar ratio \( r = U/G \) of the value obtained by the principal of propellant chemistry, \( r = 1.5 \). The Y123 samples with molar ratios \( r \) were of 1.5 named as Y123\(_1\) and 2.02 named as Y123\(_2\); and the Y358 samples with molar ratios \( r \) were of 1.4 named as Y358\(_1\), 1.5 named as Y358\(_2\) and 1.72 named as Y358\(_3\). The nitrates reactants and the fuels were dissolved in 10 mL of ultrapure water in each case and mixed homogeneously.

The color of solutions of the mixture was turquoise (Figure 1 a) and it was carried to thermal blanket type furnace. The mixture was heated until ignition temperature \( T_i \sim 390°C \) in a ramp of 10°C/min. To that temperature \( T_i \), the fuels exercise their role starting a ignition process reaching high temperature. This ignition process lasted about 1 min, after that, the samples were cooled down rapidly to room temperature. Therefore, the obtained powders for all synthesis were dark brown (Figura 1 c).

However, their respective XRD patterns showed that the powders were not totally ordered then they required heat treatment. The samples was carried out a heat treatment at 920°C in Muffa Yamato FO210CR for each samples in air and cooled down slowly to room temperature.
X-ray diffraction (XRD) was carried out to the synthesized powders after the heat treatment in order to determine the phases composition of the powders, using a Cu $K\alpha$ radiation source of Bruker D8-advance powder diffractometer. The position of peaks and intensities were obtained between 20° y 70° with a step size of 0.02. The results of XRD measurement indicate that both synthesis of Y123 samples have predominant superconducting $Y_1Ba_2Cu_3O_{7−δ}$ phase as shown in Figure 2.

The peaks in $2\theta = 47°$ indicate an orthorhombic crystal structure with simetric group $Pmmm$ according to PDF 038-1433 [10]. Also an secondary phase was observed, $Y_3Ba_8Cu_5O_{18−δ}$, which is an ordered deformation of $Y_1Ba_2Cu_2O_{6.5+δ}$ with a simetric group $P4/mmm$ [11] and small peaks corresponding to $Y_2BaCuO_5$ [12], $BaCuO_2$ (PDF 038-1402) and $CuO$ [13].

The presence of these impurity phases is due to the decomposition of the $Y_1Ba_2Cu_3O_{6.5+δ}$ phase [14] probably given post-reaction heat treatment. The $Y_3Ba_8Cu_5O_{18−δ}$ phase decreases
when it was increased the molar ratio of fuels \( r \) of 1.5 to 2.02, however, the impurity phases as green phase \( Y_2BaCuO_5 \) and \( BaCuO_2 \) increases due to greater decomposition of superconducting YBCO.

Measurement of X-ray diffraction (XRD) for the \( Y_{358} \) samples was carried out using a Co radiation source of Bruker D8-advance powder diffractometer. The positions of peaks and intensities were obtained between 20° and 70° with a step size of 0.02. In Figure 3 is shown XRD patterns of a group of \( Y_{358} \) samples which in the samples \( Y_{358} \) have a predominant phase \( Y_{123} \) with several compounds due to incomplete reactions given in the synthesis possibly due to the deficit of a urea or excess of glycine. The \( Y_{358} \) samples have better XRD patterns with two phases: \( Y_1Ba_2Cu_3O_7-\delta \) and phase green \( Y_2BaCuO_5 \), and has only an impurity corresponding to \( Y_3Ba_8Cu_5O_{18-\delta} \) phase. This samples were synthesized with \( r = 1.5 \) according to Fumo. Finally, The \( Y_{358} \) samples have only two phases, \( Y_1Ba_2Cu_3O_7-\delta \) and \( Y_2BaCuO_5 \).

![Figure 3. XRD patterns of the \( Y_{358} \) samples. Synthesized powders with \( r = 1.4 \) (cyan line), synthesized powders with \( r = 1.5 \) (red line) and synthesized powders with \( r = 1.72 \) (blue line). Symbols ▽, ■ and ○ indicate peaks due to \( Y_1Ba_2Cu_3O_7-\delta \), \( Y_3Ba_8Cu_5O_{18-\delta} \), \( Y_2BaCuO_5 \), respectively.](image)

However, it was not observed the new phase \( Y_{358} \) reported by Aliabadi [4] in any of the prepared samples with molar ratio of \( Y:Ba:Cu::3:5:8 \). S. Gholipour et al.[15] reported the coexistence of phases \( Y_{123} \) and \( Y_{358} \). In addition, it is observed that these phases have similar XRD patterns and it is not easy to distinguish by this measurement.

### 3. Results and discussions

The microstructure of the grains were determined by transmission electron microscope (TEM) (MET) TECNAI G² F20 equipped with an energy dispersive x-ray (EDX) for analysis. Samples
for transmission of electron microscopy were prepared by placing a drop of presonicated-aliquot on a carbon coated Cu grid.

![HR-TEM images of grain of Y358 sample.](image)

**Figure 4.** HR-TEM images of grain of Y358\_2 sample.

The results of TEM are in Figure 4 it was observed two grain sizes for the Y358 samples: some of 300 nm in diameter on average and others of 1.6 µm. Moreover, the same size distribution was observed in Y123 samples (Figure 5). The grain belongs to the Y123\_1 sample and its size was 2.05µmx1.36µm.

![HR-TEM images of grain of Y123 sample.](image)

**Figure 5.** HR-TEM images of grain of Y123\_1 sample.

It was carried out high resolution TEM (HR-TEM) in the marked region shown in Figure 5 b. In this figure, it was observed the crystalline planes of the material what shown that the powders have an ordered structure. It is known that Y123 phase has a preferential phase Y123 has a preferential orientation for the plains [0 0 l] and the analysis of fast fourier transform (FFT) (Figure 5 c)) confirms this characteristic of the YBCO. The lattice parameters measured by FFT were 3.84 Å y 3.86 Å, and the lattice parameters of superconducting YBCO according [10] to literature are \(a = 3.8185\) Å, \(b = 3.8856\) Å and \(c = 11.6804\) Å. Taking into consideration the measurement uncertainty, the measured lattice parameters are very close to the parameters \(a\) y \(b\) which indicate that the planes are orientated in direction [001] and the measured parameters correspond to an orthorhombic structure.
SQUID magnetometry was performed on a Quantum Design magnetic property measurement system (MPMS)-5S equipped with a 5 T superconducting magnet. Field cooled (FC) and zero field cooling (ZFC) dc magnetization were measured as a function of temperature under an applied field of $H = 100$ Oe. Figure 6 shows that Y$_{123_1}$ and Y$_{123_2}$ samples had a diamagnetic behavior in the ZFC and FC measurements. Therefore, SQUID magnetometry showed that both samples were superconducting with $T_{\text{onset}}$ of 91.79 K and 90.98 K, respectively in Figure 6). The variation of obtained $T_c$ in each sample is intimately related to the oxygen content according to M. Kogachi et al. [16]. By the obtained $T_c$ above 90 K, the oxygen content of Y$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ is estimated to be $\sim 6.9$.

![Figure 6](image1.png)

**Figure 6.** ZFC y FC magnetization of Y123 samples as a function of temperature under $H = 100$ Oe.

It was considered the influence of other secondary phases found by XRD in the magnetization or magnetic moments measured in all sample volume, however, those phases are not superconducting. Therefore, they do not contribute significantly to the measured magnetic moments, except the BaCuO$_2$ phase which has been reported that decrease diamagnetic signal. For that reason, it was observed that magnetization curves are greatest slope and have greater magnetization for below temperature of $T_c$ when synthesis was $r = 1.5$ (Y$_{123_1}$) due to it has less concentration of BaCuO$_2$.

![Figure 7](image2.png)

**Figure 7.** ZFC and FC magnetization of Y358 samples as function temperature under $H = 100$ Oe.

Additionally, the ZFC and FC measurements of Y358 were shown in Figure 7. The best sample has a $T_{\text{onset}}$ of 91.77 K which was synthesized by molar ratio $r = 1.5$. However, the
contribution of incomplete reaction was observed decreasing diamagnetic signal in the magnetic measurement for the Y358, although, it has a good critical temperature $T_c \sim 89.7 \text{ K}$. On the other hand, magnetic measurements of Y358 sample has a poor oxygen content on samples. That is the reason why the samples have a low critical temperature $T_c \sim 82.8 \text{ K}$.

Konne et al. [6] synthesized nanowires of YBCO which identified as new Y358 phase, however their samples has low critical temperature $T_c \sim 90 \text{ K}$. They justified the difference between the literature onset $T_c$ values for Y358 is likely due to morphology effects such. In spite of the fact that most grains observed by TEM have an average size of 300 nm, these powders do not suffer the effects of morphology and maintain their critical high temperatures $T_c \sim 92 \text{ K}$, Figure 6-7.

The electrical transport measurement was carried out measuring the resistivity as a function of temperature by the dc four-point method on sample Y123 inside a Dewar with liquid nitrogen and helium. In order to perform this measurement it was needed to compact the synthesized powders in order to get a pellet and it was applied a heat treatment again at 920°C for 2 h in air. Then the pellet was cut to get a slab of $5.8 \times 2 \times 1.22 \text{ mm}^3$. Figure 9 shows the electrical resistivity dependence on temperature, it was observed that the Y123 sample has a superconducting transition with a prolonged slope. The superconducting transition temperature $T_{c,\text{trans}}$ was 90.7 K. The resistivity at room temperature was 6.44 Ωmm which was too big and tended to increase until $T_c$ temperature. This contrasts with other reports where they got lower values of resistivity.

![Figure 8](image_url)

**Figure 8.** Measurement of electrical transport by the dc four-point method on the Y123 sample.

The great value of measurement of resistivity and the prolonged slope could be explained by the bad percolation of current inside the sample as a consequence of grain coalescence or the impurities presence. This slab was oxidized by atmosphere of $O_2$ at 460 °C for 6 h and the measurement of electrical transport showed that the effect of oxidation atmosphere did not have a significant contribution in sample.

4. Conclusions
We have successfully demonstrated that using this modified combustion in solution method using mixture urea-glycine for first time, it is possible to prepare fine powder of $Y_1Ba_2Cu_3O_{7-\delta}$ phase at temperatures as low 920 °C. We have showed that process of YBCO phase formation is highly dependent of the molar ratio urea/glycine. The measurements of ZFC and FC were obtained $T_c \sim 92 \text{ K}$ when the reaction was with molar ratio $r = 1.5$ for the Y123 and Y358 samples. We have not observed the new Y358 phase in any of prepared samples. The measurement of
electrical transport was found $T_c \sim 91$ K. The obtained $T_c$ above to 90 K is in according to oxygen content of 6.9. Although most grains have an average size of 300 nm, these powders do not suffer the effects of morphology and maintain their high critical temperatures $T_c \sim 92$ K.

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