Structural characterization of the YBa$_2$Cu$_3$O$_{\sigma}$ superconductor with phases [$\sigma$=6.87,6.89 and 6.9] obtained by solid state reaction

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Abstract— The YBa$_2$Cu$_3$O$_{\sigma}$ superconductor was obtained by solid-state reaction through thermal treatments without the need to use a controlled atmosphere composed of inert or reactive gas. To obtain the superconducting phases, oxygenation treatments were carried out, with the incorporation of oxygen from the open air atmosphere to the sample in periods of 6 hours. Through X-ray diffraction characterization, the YBa$_2$Cu$_3$O$_{\sigma}$ superconducting phases were identified with [$\sigma$ = 6.87, 6.89 and 6.9] in the sample. There was no presence of non-superconducting phases, nor elements not corresponding to stoichiometry. This was confirmed through Raman spectroscopy and SEM-EDS. The Meissner effect test was performed on the sample, allowing magnetic levitation to be observed, confirming the obtaining of the superconductor.

Keywords— YBaCuO superconductor, solid-state reaction, superconducting materials.

I. INTRODUCTION

Superconductivity is attributed to the phonon-electron interaction in materials at low temperatures, reducing vibrations within the crystal lattice and allowing free movement of the charge carriers. This effect results in zero electrical resistance. Another property that superconductors show is diamagnetism, caused by the interaction of magnetic fields with the superconductor, allowing the formation of surface supercurrents that generate a magnetic field opposite to that applied to them [1], [2]. The superconducting state manifests at a critical temperature (Tc) which depends specifically of superconducting material.

Since Onnes' contributions [3], different superconducting materials have been obtained until reaching compounds based on copper oxides, in addition to the development of microscopic theories such as that of Bardeen, Cooper and Schrieffer that show the quantum behavior of superconductors under a given Tc [4], [5].

High-temperature superconductors (HTS) contain copper and oxygen atoms in their unit cell, because they form the CuO$_2$ crystalline planes [6], facilitates electronic movement at low temperatures, however, this occurs when there are deficiencies of oxygen in the unit cell. As a result of the above, changes in the unit cell are generated by modifying its dimensions and crystal arrangements with variations in the CuO$_2$ planes, obtaining Tc values close to 273 K [6]. The YBa$_2$Cu$_3$O$_{x}$ stands out among superconductors because it has been reported to exhibit superconductivity at Tc= ~ 90 K, with the ability to interact with magnetic fields of up to 674 T [6]. In addition, this superconductor in comparison with other materials achieves the formation of high magnetic fields at higher temperatures than BiSrCaCuO, BiPbSrCaCuO, MgB, NbSn and NdFeAsF as reported in [7]. The YBa$_2$Cu$_3$O$_{x}$ superconductor presents different phases of superconductivity related to the amount of oxygen in an interval of x= (0≤ x ≤ 0.65) [8]. Its most common applications are in electrical and electronic devices [9]–[11] transmission systems, power and ripple energy [12]–[18], microwave transmission components and instruments [19], etc. Therefore, work must be done on improving the processes for obtaining the YBa$_2$Cu$_3$O$_{x}$ superconductor in greater quantities and without degrading its electromagnetic properties (zero electrical resistance and diamagnetism), to facilitate its application in optimizing a greater number of electromechanical devices. In addition, using YBa$_2$Cu$_3$O$_{x}$ reduces operation - maintenance costs in the use of liquid nitrogen compared to the use of liquid helium.

Commonly, a sample of superconducting YBa$_2$Cu$_3$O$_{x}$ obtained by solid state synthesis shows a mixture of superconducting phases that depend on the parameters of heat treatments [20]–[26] undergone in controlled atmospheres. Several authors report that, to obtain YBa$_2$Cu$_3$O$_{x}$ by solid state reaction, more than two thermal cycles must be carried out, these are from 8 to 100 h, moreover, a system in which a special atmosphere of oxygen has to be supplied under specific conditions of flow, pressure and time [27]–[33].

This work focuses on synthesizing YBa$_2$Cu$_3$O$_{x}$ superconductors without the use of a controlled atmosphere (in open air) and with shorter processing times compared to those reported.

II. METHODOLOGY

The bulk superconducting YBa$_2$Cu$_3$O$_{x}$ was obtained by solid state reaction using the precursors Y$_2$O$_3$, BaCO$_3$, CuO, with 99.99% purity in each. The precursors were mixed and the first heat treatment was carried out at 1178 K for 12 hours. The second heat treatment was carried out at 1173 K for 12
hours, immediately an oxygenation treatment (in open air) was carried out at 673 K for 6 hours. The third treatment was performed at 1173 K for 12 hours, and an oxygenation treatment (in open air) was continuously performed at 723 K for 6 hours. The fourth heat treatment was done at 1193 K for 12 hours. The fifth heat treatment was performed at 1198 K for 12 hours. The bulk form was obtained through cold pressing with a diameter size of 12.7 mm. The last heat treatment was at 1193 K for 6 hours.

Pressed sample was characterized using X-ray diffraction (XRD) with a Siemens D5000 XRD using Cu-ka radiation as X-ray source (1.5406 Å), in the $2\theta$ range 20° to 80°. The surface morphology was observed by a scanning electron microscope (SEM) in a Field emission Jeol equipment model JSM-7401F, the quantification of the atomic concentration was carried out by means energy dispersion spectrometry (EDS) with an acceleration voltage of 20 kV for EDS and 5kV for SEM. In addition, Raman spectroscopy measurements were carried out in a Raman Thermo scientific DXR2 system employing an excitation line of 633 nm.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

The superconducting phases identified in the sample are YBa$_2$Cu$_3$O$_{6.87}$, YBa$_2$Cu$_3$O$_{6.89}$ and YBa$_2$Cu$_3$O$_{6.9}$, and were compared with the powder diffraction files 87-1477, 87-1469 and 87-1359 respectively, and are seen in Fig. 1. The formation of non-superconducting phases was not identified in the diffractogram.

The average crystal size in the sample was determined from the Scherrer-Debye equation (1) and Williamson-Hall (2) for the most prominent signals.

$$d = \frac{k \lambda}{FWHM \cdot \cos \theta}$$

(1)

$$FWHM \cdot \cos \theta = \frac{k \lambda}{d} = \varepsilon \cdot \sin \theta$$

(2)

In equations (1) and (2), $\theta$ corresponds to the Bragg angles in the diffraction signals, $\lambda$ has the value of 1.5406 Å which is the wavelength of the X-ray emission source, $\kappa = 0.93$ which is the value of the shape constants and $d$ is the crystal size.

The average crystal size obtained by (1) is 56nm ± 14nm, and it is a lower value than that obtained by (2), which is 79nm. This result is attributed to the fact that in the Williamson-Hall methodology, the contributions of the stresses in the crystal lattice and particle sizes are considered as a linear combination. However, this obtained value is very similar to that obtained by Oku [34] and is considered favorable for its electrically conductive properties [31]. Furthermore, the variation in the crystal size obtained by (1) and (2) is attributed to the diffusion during the heat treatments that were carried out at high temperatures, below the fusion point.

An analysis was performed with the Material Data Jade software between the indexed powder diffraction files of the superconductors phases obtained and the results obtained in the X-ray diffraction pattern, showed a belonging to a group space Pmmm (47) with the parameters network: $a = 3.8421 \, \text{Å}$, $b = 3.8897 \, \text{Å}$ and $c = 11.6742 \, \text{Å}$, $\alpha = \beta = \gamma = 90^\circ$ [35].

B. Raman spectroscopy

Fig. 2 shows the atomic arrangement in the unit cell of the superconductor YBa$_2$Cu$_3$O$_6$, defining the typical positions of the Cu (2), O (2) and O (3) atoms, forming the CuO$_2$ planes. In addition, the bond of the CuO chains formed by the Cu (1) and O (1) atoms is observed in orientation parallel to the b axis. The CuO chains are linked by the O (4) oxygen atom with the CuO$_2$ planes.

The YBa$_2$Cu$_3$O$_6$ superconductor has polarized vibrations on different axes and active Raman modes $5A_g + 5B_2g + 5B_3g$ in its orthorhombic array [36]–[38]. Additionally, this HTS superconductor typically presents a phase recombination caused by the amount of oxygen present in their respective unit cells, causing shifts in their vibrational modes attributed to network stresses. This typical behavior is observed in the Raman spectroscopy of the sample obtained in Fig. 3. The modes corresponding to $A_g$ symmetry belonging to the Ba bonds at ~ 110 cm$^{-1}$, Cu$_2$ at ~ 142 cm$^{-1}$, O$_2$ and O$_3$ bonds are antisymmetric vibrations at ~ 335 cm$^{-1}$.
Additionally, there are also the symmetrical vibrations of the $O_{2,3}$ bonds at $\sim 443 \text{ cm}^{-1}$, which are referenced to the characteristic planes of CuO$_2$ where supercurrents are formed.

At $\sim 499 \text{ cm}^{-1}$ the vibratory mode bond between the CuO$_2$ planes and the CuO chains corresponding to O$_4$ are identified. Jointly, vibrational modes were identified in ($\sim 174$, $\sim 200$, $\sim 220$, $\sim 245-253$, $\sim 275-289$, $\sim 380-396$, $\sim 417-420$, $\sim 529$, $\sim 567$, and $\sim 584-604 \text{ cm}^{-1}$) and that are attributed to defects in the crystal lattice caused partial oxygen vacancies and phase mixing [36]–[45].

![Raman spectra](image)

**Fig. 3.** Raman spectra of the sample YBa$_2$Cu$_3$O$_\sigma$ with superconducting phases ($\sigma = 6.87, 6.89$ and $6.9$).

**C. Morphological characterization (EDS-SEM)**

EDS analysis in Fig. 4, allowed determining the average atomic percentage for the elements present in the sample, obtaining 5.04% for Yttrium, 15.91% for Barium, 23.12% for Copper and 55.93% for Oxygen, corroborating the results obtained with X-ray diffraction and Raman spectroscopy in the absence of other elements. The oxygen content in a superconductor modifies the dimensions of the unit cells, causing phase mixing and an alteration in their structural characteristics that intervene in the electrical properties [31].

![EDS analysis](image)

**Fig. 4.** Analysis by SDS superconductor YBa$_2$Cu$_3$O$_\sigma$ sample.

In Fig. 5 the SEM images of the sample YBa$_2$Cu$_3$O$_\sigma$ with superconducting phases are shown, where it is possible to observe on the surface of the sample an agglomeration of grains with different measures, with the presence of small porosities. The minimum particle size was $\sim 0.12 \mu\text{m}$, with a maximum particle size of $\sim 13.6 \mu\text{m}$ and an average of $\sim 7 \mu\text{m}$. The existence of large particles decreases the boundary limits and benefits the increase in electrical conductivity [31]. The development of heat treatments at a temperature greater than 1173 K, facilitates the formation of large crystals, which in turn will form large grains due to a coalescence process in the agglomeration.

![SEM images](image)

**Fig. 5.** SEM images of the sample YBa$_2$Cu$_3$O$_\sigma$ with superconducting phases ($\sigma = 6.87, 6.89$ and $6.9$), a) measurement on a scale of 10 $\mu\text{m}$ and b) measurement on a scale of 1 $\mu\text{m}$.

The superconductor YBa$_2$Cu$_3$O$_\sigma$ sample was cooled using liquid nitrogen in order to decrease the temperature to 77 K and then a neodymium magnet was approached. The sample presented the so-called Meissner effect, verifying the superconductor diamagnetism, as shown in Fig. 6.

![Meissner effect](image)

**Fig. 6.** Meissner effect of the sample YBa$_2$Cu$_3$O$_\sigma$ with superconducting phases ($\sigma = 6.87, 6.89$ and $6.9$)

**IV. CONCLUSIONS.**

The synthesis was developed with six thermal treatments and two oxygenation treatments to obtain the superconducting
sample YBa2Cu3Ox in open air, i.e. without the need for a controlled special atmosphere, presenting superconducting phases YBa2Cu3Ox.87, YBa2Cu3Ox.89 and YBa2Cu3Ox.9 identified through the structural analysis by the X-ray diffraction pattern, obtaining an average crystal size of 67 nm.

The analysis by Raman spectroscopy allowed to identify the characteristic vibrational modes of the YBa2Cu3Ox; and together with the EDS analysis, atomic percentage values were obtained according to the stoichiometry for the elements that make up the superconductor, allowing to corroborate the absence of other elements unrelated to this compound.

The obtaining of superconducting phases is due to the performance of thermal treatments with temperatures close to 1173 K. The SEM images show the growth of grains is promoted at the expense of the smaller ones, reducing the amount of pores. The Meissner effect test was developed with an NdFeB magnet, allowing the effect of magnetic levitation to be observed due to the diamagnetism generated in the superconductor at cryogenic temperature.

Finally, with the structural characterizations carried out on the sample, and the Meissner effect test, it is recommended to perform the electrical characterization analysis using the four-point technique to determine the Tc of this superconductor; allowing to have a point of reference for future experiments with the impurification of this material.

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V. REFERENCES


