Synthesis and Caracterization of CCTO ($CaCu_3Ti_4O_{12}$)

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ABSTRACT

The objective of this work is to study the ceramic material CCTO ($CaCu_3Ti_4O_{12}$) by X-Ray Diffraction. The CCTO is a material with a giant dielectric constant at room temperature and good temperature stability over a wide temperature and frequency ranges. The preparation method has a great influence on the structure and dielectric properties of this material. The CCTO was prepared by solid state method in a planetary high energy ball milling (Fritsch Pulverisette 5). Stoichiometric quantities of $CaCO_3$ (Aldrich 99%), TiO_2 (Merck 99%) and CuO (Analar 98%) were dry milled during 30h with a rotational speed of 370 rpm and then calcined at 1050 ºC for 12h. After, the CCTO was studied by X-ray diffraction (XRD). The refinament showed that the CCTO was formed with 100% mass, the graph of Williamson-Hall showed a homogeneous sample, with a contraction in the crystal lattice and a reasonably small particle size.

Keywords: solid state method, X-ray diffraction, refinament.

INTRODUCTION

The rapid growth of the wireless communication industry has created a high demand for the development of small size, low power loss, and temperature stable microwave components [(1)]. Ceramic materials are extensively used in the electronics industry due to its high durability when exposed to extreme conditions. In addition, we will seek to increasingly electronic devices faster, smaller and efficient, requiring the use of materials that have high dielectric constant, a necessary requirement for memory devices.

Materials with the ε > 103 are considered materials with high dielectric constant (ACD), which is very important for the development in technology of electronic devices smaller such as memories [2], gas sensors, many others. Such materials must be stable in a wide temperature range and frequency, and have low loss dielectric [3].

The CCTO (Copper Titanate and Calcium or Tetratitanatotricobre) has advantages over other ceramic materials used in dielectrics, for instance, SrTiO3 and BaTiO3 by simple processing, despite being very sensitive to processing [3]. In addition, this compound is not viable industrially by doping need and have a less complex than SrTiO3 or BaTiO3, which require high temperatures, reducing atmospheres, limits diffusion of oxygen and dopants along the grain boundary. The CCTO is a very interesting material because it has several properties: dielectric, varistor, gas sensor and resistive memories among others. Because of its great scientific and technological development is necessary to analyze the behavior of this material with small microstructural changes [4]. Through the X-ray diffraction is possible extract information about the structure of the material, where the technique of x-ray diffraction crystalline phase with the Rietveld refinement allows theoretically to confirm the structure and crystallographic information of the sample in powder form [5].

MATERIALS AND METHODS

In this work, samples of $CaCu_3Ti_4O_{12}$ was sintered from powders of $CaCO_3$ (Aldrich 99%), TiO_2 (Merck 99%) and CuO (Analar 98%), using the conventional solid-state reaction method. Oxides and carbonate were weighed and then the mixture was high-energy ball milling during 30h in a planetary ball mill (Fritsch Pulverisette 5). The rotation speed of the disks carrying the sealed vials was 370 rpm. This operation was used to improve the homogeneity of the powder. Then the powder was calcined at 1050 ºC for 12h.

X-ray diffraction

The X-ray powder diffraction profiles of the samples were recorded using a powder X-ray diffractometer system Panalytical, model X´Pert MRD. Powder samples were fixed on a silicon plate with silicon paste. Patterns were collected

at laboratory temperature (about 294 K) using Co - Kα radiation, operated at 40kV and 30mA, with five seconds for each step of counting time along angular range 10-80 (2θ). In the present study is adopted the Rietveld's powder structure refinement analysis [6, 7, 8] of X-ray powder diffraction data to obtain the refined structural parameters.

Scherrer equation

The Scherrer equation is currently the most widely used equation to calculate particle size through the FWHM (Full Width at Half Maximum) of diffraction peak, where it has a simplified way to calculate the particle size. For the beam divergence caused by experimental conditions (instrumental factor) of equipment and non-uniformity of particle sizes, which considerably affects the width of the diffraction peaks do not affect the calculations of particle sizes and micro-deformations, it is necessary measure the performance of a standard sample of particles with large sizes and homogeneous [5].

The calculation of particle size, *L*, was made in the program DBWSTool2.3.exe using the Scherrer equation [9],

$$L = \frac{k\lambda}{\beta \cos\theta} \qquad (A)$$

where ***k*** (constant value 1) is the shape coefficient, ***λ*** is the wavelength, ***β*** is the peak full width at half maximum (FWHM) of each phase and θ is the Bragg angle. The parameter ***β*** was corrected for instrumental width using the following equation:

$$\beta = \sqrt{\beta_{exp}^2 - \beta_{inst}^2} \qquad (B)$$

where $\boldsymbol{\beta}_{\mathbf{exp}}$ is the experimental width and $\boldsymbol{\beta}_{\mathbf{inst}}$ instrumental width that are extracted from a sample pattern of LaB_6 [10].

Williamson-Hall equation

Another classical method to obtain quantitative information on particle size and microstrain considering the enlargement of the diffraction peaks is through the Williamson-Hall plot [5].

The Williamson-Hall plot allows us to extract the microstrain through the angular coefficient (slope of the curve), and mean particle size using the linear coefficient (the intersection of the curve with the ordinate axis), and their homogeneity from the angular width of peak diffraction is represented by the following equation [11]:

$$\frac{\beta \cdot \cos\theta}{\lambda} = \frac{k}{D} + \frac{4\varepsilon}{\lambda}\operatorname{sen}\theta \qquad (C)$$

where ***β*** is the half width of diffraction peak (FWHM), ***λ*** is the wavelenght of x-rays and ***K*** is a constant (value 1) which determines the point in the network reciprocal, ***D*** is the average size of crystallite, ***ε*** is the microstrain.

RESULTS AND DISCUSSIONS

To perform the refinement was used DBWSTools 2.3.exe program and ICSD (Inorganic Cristal Structure Database) [8]. After the refinament, when calculated the particle size by the equations (A) and (B) the DBWSTool2.3.exe program also provided the values necessary to plot the graph FWHM and Williamson-Hall. The XRD pattern of CCTO with their refinament and family of crystallographic plans is shown in Fig. 1. It was noted that the sample showed no secondary phases, having formed only $CaCu_3Ti_4O_{12}$ cubic.

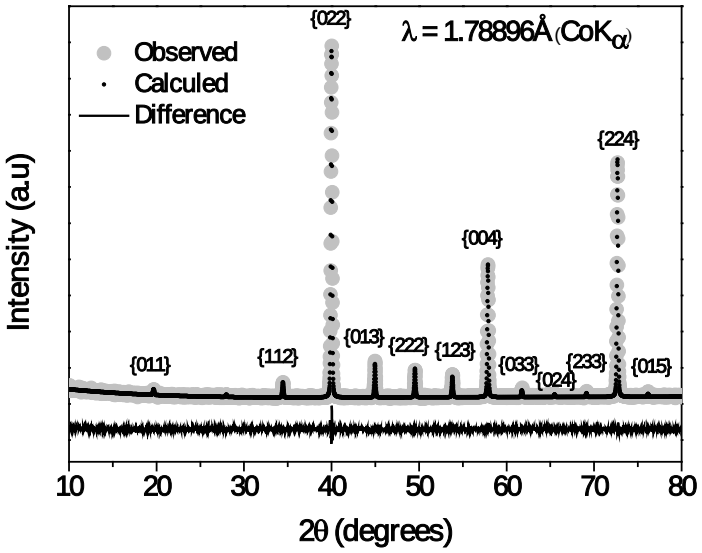

Figure 1. XRD pattern of CCTO with their refinament and family of crystallographic plans.

Some parameters of the refinament are shown in Table 1. As the factor R-WP is the most significant statistical factor among all factors which best reflects the progress of refinament, since its analytical expression involves the method of least squares [12], the value found for it was very good because are usually considered satisfactory values between 10-20%. Another factor that presented a satisfactory value was S, being 1 (one) the standard value to classify the refinament as appropriate [8], and in the refinamento of CCTO, the value was lower than expected.

Table 1 - Values of some parameters of the refinament for the CCTO

% R-WP	% R-EXPECTED	S	% MASS
7.80	8.77	0.89	100

The results of crystallite size are presented by family crystallographic planes and the average of these values can be seen in Table 2. It is possible to verify a difference in particle size on the crystallographic planes, the value of the average size found showed that the sample has a reasonably small particle size.

Table 2 – Particle size by Scherrer for the CCTO

Particle size (nm)	
Family of crystallographic planes {hkl}	
{011}	57.4 (3)
{112}	62.3 (3)
{022}	64.4 (3)
{013}	66.2 (3)
{222}	68.2 (4)
{123}	69.9 (4)
{004}	71.7(4)
{033}	73.1 (4)
{024}	74.6 (4)
{233}	76.2 (4)
{224}	77.5 (4)
{015}	78.4 (4)
Average size	70.0 (4)

The graph FWHM as a function of the angle 2θ is shown in Fig.2, where the particle size does not vary as homogeneous, which was expected, since despite the Scherrer equation be calculeted using the LaB_6 standard sample, it does not take directly into account the microstrain in their calculations of particle size as the equation of Williamson-Hall.

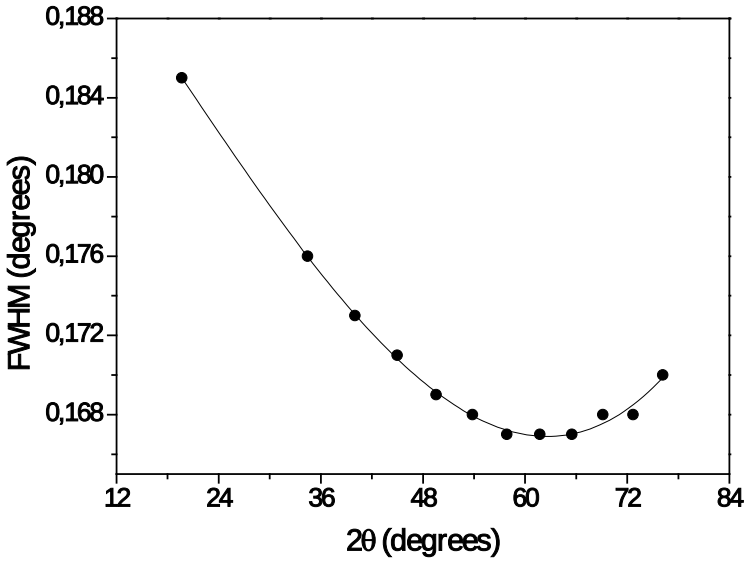

Figure 2. Graph FWHM of CCTO as a function of the angle 2θ.

The graph Williamson-Hall as a function of the sen θ is shown in Fig. 3, that presents a straight decreasing, indicating a homogeneous sample, but with microstrain negative, representing a contraction in the crystal lattice. Using equation (C) was calculated value of crystallite size and microstrain, respectively by a linear and angular coefficient of straight graph Williamson-Hall.

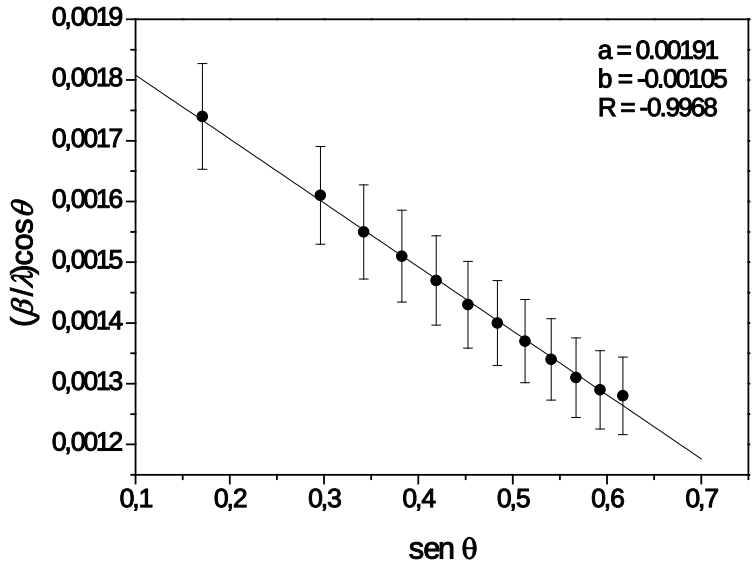

Figure 3. Graph Williamson-Hall of CCTO as a function of the sen θ.

The microstrain and the comparison of the average particle size by Scherrer and Williamson-Hall can be seen in Table 3. The microstrain value is close to zero. This value is much smaller than that for the microstrain value of 0.01% obtained for standard Si powder that is free of any microstrain, indicating that the CCTO is not experiencing any microstrain [13]. There is a difference between the values of average particle size obtained by Scherrer and Williamson-Hall. This is because the sample did not show homogeneity, as can be seen in Fig. 2, which presents a parabolic distribution [11].

Table 3 – Microstrain and average particle size by Scherrer and Williamson-Hall

Microstrain (%)	Average particle size (nm)	
	Scherrer	Williamson-Hall
-4.82×10^{-4}(3)	70.0 (4)	51.13(3)

CONCLUSIONS

The refined sample showed R-WP and S satisfactories, where the S value was less than 1 (characteristic of the sample), and R-WP proved to be even better than they normally are considered satisfactory, which is between 10% and 20 % [8]. The Fig. 1 shows that the calculated part was very close to the measured (observed), resulting in a difference of least squares without much variation [6]. Thus, it was confirmed by refinement using DBWSTool2.3.exe that there is only one phase present the $CaCu_3Ti_4O_{12}$ (CCTO). The average particle size calculated from Williamson-Hall had a value lower than that calculated by Scherrer. Despite this, the values are considered reasonably small. The CCTO is not experiencing any microstrain.

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