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Comparison of conventional and non conventional methods of synthesis for the superconducting Ba-Pb-Ca-Cu-O system

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The methods for the synthesis of the superconducting systems are the well known usual and the unusual. Usual methods are the classical heating in furnace (oven) known as conventional methods for the ceramic samples. Special extra furnace techniques are used as firing profiles with different heating rates as for example, 5° C/min, or N° C/min or cooling at any rate, too. The unusual methods or non conventional methods begin with: films with depositions of components [1], thin films technology [2], metallurgical route for synthesis [3], thin films deposited by sol-gel process on different substrates [4], sintering [5], spray deposition [6], films deposited by spray pyrolysis method [7], solid-state reaction [8], thin films by pulsed laser deposition [9], sol-gel process [10], composites obtained by in situ spray pyrolysis method [11] and et al. Classical mixture with the general chemical formula $Ba_{(3-x)}Pb_xCa_2Cu_3O_{8+d}$ (x=0.2) according to the general Ba-Pb-Ca-Cu-O system, was prepared either with the classical conventional oven and with an microwave oven [12]. The comparison of the two methods shows that there are very interesting differences.

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Keywords: Superconductors, Crystal structure, Microwaves, Non conventional synthesis

1. Introduction

The Bardeen-Cooper-Schrieffer (later known as the BCS Theory after their initials) model, [13] at 1957, explains "conventional" or "low-temperature" superconductivity in metallic solids. Finally they showed at their 32 pages, paper for the first time that, after a sufficiently low temperature (which is the critical temperature T_c), electrons near the Fermi energy join with relatively distant electrons with opposite momentum and spin to form Cooper pairs with no net momentum or spin.

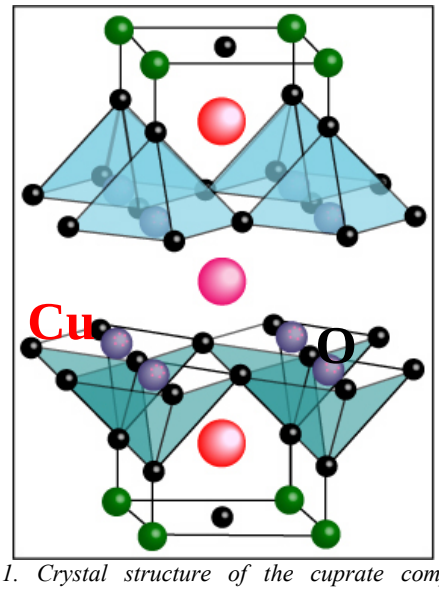

Fig. 1. Crystal structure of the cuprate compound $Bi_2Sr_2CaCu_2O_{8+\delta}$, or Bi2212, showing the copper (purple) and the oxygen (black) layer.

This pair, named Cooper pair due to a very weakly attractive force between the electrons that arises as they interact with lattice vibrations (phonons). Bosons with identical quantum numbers, the pairs condense into the coherent superconducting state. The explanation is different in the cuprate HTSCs.

Bednorz and Müller, in 1986, from IBM-Zürich discovered superconductivity at 35 K in copper oxide [14]. In 1987, Chu discovered an yttrium-barium-copper oxide which is superconducting at 93 K, ($YBa_2Cu_3O_7$) above the temperature of liquid nitrogen and of course until then, the highest temperature at which superconductivity has been observed has been pushed to 134 K for some exotic rare earth compounds (Service 1996). Except this table a lot of new materials are present every International or National Congress on Materials [15],[16],[17]. In bulk materials the transition temperature T_c of magnesium diboride (MgB_2) is only exceeded by the much more complicated perovskite cuprate structures. The new discovery provides a salutary reminder of the richness of the solid state and the way that interesting physics can emerge from quite unexpected areas [18]. Superconductivity has found recently in new areas unexpectable such as, in single crystals made of carbon-60 or polymers [19]. The chemical equation between the oxides of the first HTS superconductor is written below:

$$Y(OH)_3 + 2BaCO_3 + 3CuO \rightarrow YBa_2Cu_3O_7 + 3/2\ H_2O$$

The discovery of materials with HTS into the last years can be seen in the next picture where we can easily see that the YBaCuO system is at the vertical region of the

figure saying that the increasing of the Tc temperatures is work of this curious point. Additionally all these materials were antiferromagnetic as Abirkosov and Gor'kov showed that magnetic impurities dispurt superconductivity and depress Tc [20],[21].

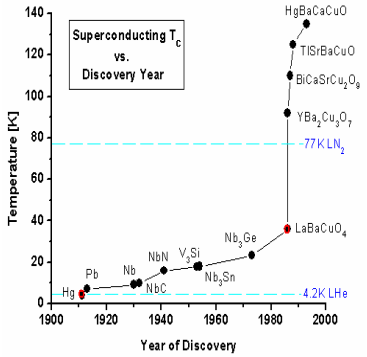

Fig. 2. The discovery of the HTS superconducting materials from 1900 until 2000.

The methods for the synthesis of the superconducting systems are the classical heating in furnace, known as **conventional methods** for the ceramic samples with or without extra systems as for example with Oxygen flow or with Ar or other gas. The ways of cooling are different and a lot of methods are required, as special electronic equipments basically for the time measurement and the ways that the temperature falls down. All these techniques make a profile in heating and cooling at any rate which is very important because of it's meaning in the manufacturing state when the product becomes commercial.

In this study as **conventional method** corresponding to a general chemical series $Ba_{(3-x)}Pb_xCa_2Cu_3O_{8+d}$ (where x=0.2,…., 1.0) the samples are prepared from oxides or salts of component elements Ba, Pb, Ca, Cu, in suitable proportions, **by heating in air**, at high temperatures according this chemical equation:

The chemical equation for the formation of the final mixture is:

$$(3-x)\cdot BaO+x\cdot PbO+2\cdot CaO+3\cdot CuO\rightarrow Ba_{(3-x)}Pb_xCa_2Cu_3O_{8+d}$$

The purities of the oxides are: 99.99% and the solid state reaction occured at free atmosphere with the oxygen of the air.

The non conventional methods that we used were by irradiation with a microwave oven. Results about the chemical synthesis about the mixtures, with the method of microvave oven, were analysed in the case of the superconducting compound $YBa_2Cu_3O_7$, by D. R. Baghurstet al [22] and A. Agostino et al [23]. On these facts, we have applicated on this method for composing of materials, which present interesting similarities and differences with the classical methods. This happens because they show the same results as the conventional methods for materials with high temperature superconductors (HTS) without the increasing temperature at high numbers and not for the same time, which is a lot of time for every experiment.

2. Experimental

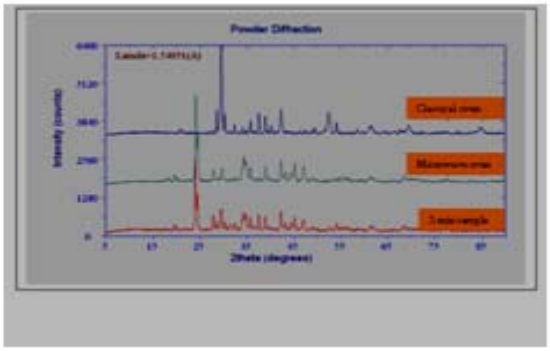

Fig. 3. XRD diagrams (CuKa radiation) of the two teams of samples at 860 ^oK.

The examination of the crystalline phases that produced by the two methods that we mentioned in the Introduction, by heating in a classical,conventional electrical oven and by the irradiation by a microwave oven are the experimental results that we introduce next. Comparison of the new methods with classical, demands the two corresponding original mixtures to be at the same initial conditions for the same original point. As were prepared the same initial chemical proportions, in Applied Physics laboratory, by mix of BaO, PbO, CaCO3, and CuO, as starting materials, according to the general chemical formula:

$$(3-x)BaO+xPbO+2CaCO_3+3CuO\rightarrow Ba_{(3-x)}Pb_xCa_2Cu_3O_{8+x}$$

where x=0.4,we made twelve (12) samples of the same initial conditions.

The first team of th six (6) mixtures were irradiated in the microvave oven for 5 min, in air, up to red-hot. The microwave oven that we used had a power at the level of P=800 W and frequency f=2.45 GHz and after the irradiation it was cooled always at the room temperature by opening at the free atmosphere. In order to succeed good homogenization, the samples were repowdered and reheated, for 60 min, in the same microwave oven, under the same conditions. After each heating in the microwave oven the sample was measured, at room temperature, by an X-Ray diffractometer, with Bragg-Brentano geometry (θ-2θ) and CuKα radiation, in a range of 2θ from 5 to 90 degrees. The second team of six (6) samples (or mixtures) were prepared by heating in a conventional electrical furnace, at 870 ^oC, for 40h and were measured by the same X-Ray diffractometer, under the same conditions. XRD diagrams for these two teams are given in the Fig. 1. When the samples are heated by the classical way at a furnace, become powders, but when they are at the microwave

oven, they obtain more solid texture. So after the measurements by the XRD, rays the samples must become again powders. This is easily with special treatment until they become again powders.

3. Results and discussion

XRD measurements is the next step after the experimental part of the procedure in either the two methods. XRD patterns which are shown at Fig. 3, at 860 ^{o}K are plotted and studied by the help of the program PLOTPOW [24]. In this Fig. 3, at the total plot the diagrams 1 (5 minutes at the microwave oven) and 2 (60 minutes at the microwave oven) are very similar for all of the frequencies from 5 until 90^{o} (for the 2θ angle). The only differences that we observe at 1 and 2 plots are at the small angles at 20^{o}(=2θ) ,20.1,20.2,18.1,17.9. The gradient from the angle 5 until 9 ^{o} is more sharp when we have the samples in the microwave oven for little time (5 min is the curve 1). As we see from the 1,2,3 curves there are differences between the 3 and the others and they are quite serious. Additionally the program EVAWIN [25] and the PDF2 [26] database, are used for the characterization and the evaluation of the samples that we had.

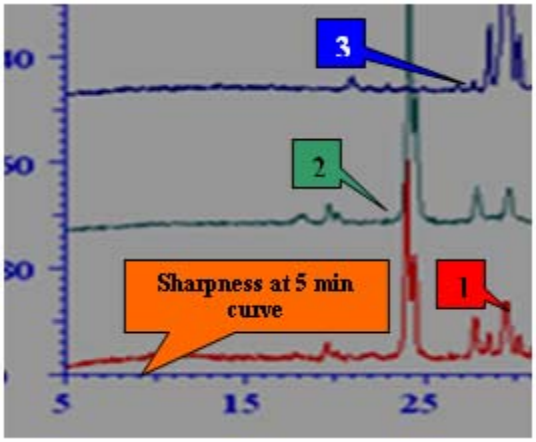

Fig. 4. XRD measurements at 860 ^{o}K, 1,2,3 are classical curve, 2 microwave curve at 60 minutes and 3 is microwave curve in 5 minutes.

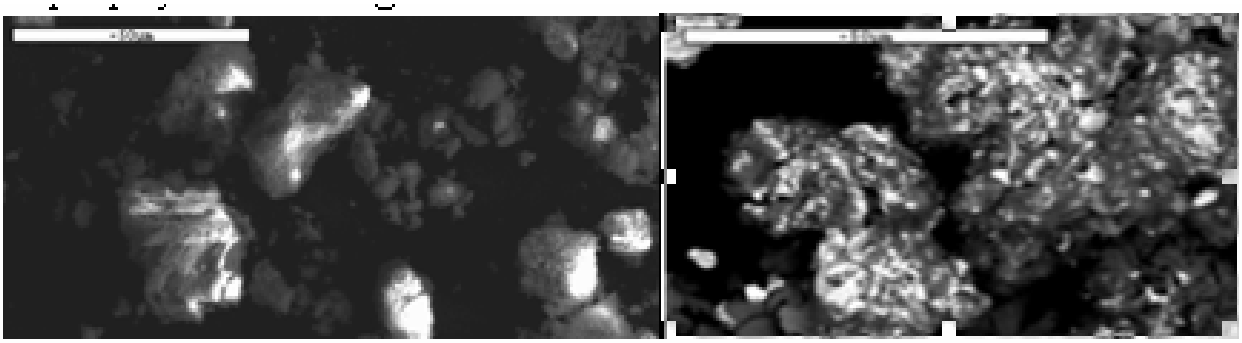

Fig. 5. SEM photos of the samples to a) conventional method (classical methods at normal furnaces at 860 ^{o}K) β) non conventional method (microwave oven method at 60 minutes).

The phases that we defined for the first sample, S01, until the sixth iSO6 in the classical furnishing and for 40 hours time, were six,6:$BaCO_3$, CaO, CuO, $BaCuO_2$, $BaCu_2O_2$ and Ba_2CaPbO_6) [27,28,29,30,31,32].

Phases for the microwave method, for the S07 until S12 samples and for 60 minutes time procedure, were $BaCO_3$, $BaPbO_3$,CuO and Ba_2CaPbO_6 [27,33,29,32]

The defined phases are shown in Table 3 and the main phases of the 12 samples is: Ba_2CaPbO_6. Using SEM analysis on the total of the samples, we found that the finale microstructure has constituted by a high distribution grain sizes 5 μm to 15 μm, as shown in Fig. 5. The grains that we observe act as "nucleation" systems in micrometer scale with circular shapes of the atoms that are collected there in scraggy surface.

Results based on the diagrams and after the refinement with the powder profile analysis (Rietveld's method), are plotted in Figs. 6, where the diagrams of Io and Ic as functions of the 2θ angle are shown and the degree of agreement between the Io and Ic is shown with the diagram of Io-Ic, which is transposed differential.

The refinement of the phases [33] is based on the initial values of the crystal structure parameters which are: 1) the space group, 2) the unit cell parameters and 3) the atomic coordinates of the phases which have been defined for all the samples and taken from the bibliography and the database ICSD [34].

The structure parameters refinement is made by the program DBWSWIN [35], which is an edition of the program DBWS9411 [36] for Windows, based on the profile analysis, known as Rietveld's method [37], improved and enhanced by DBWSPLOT which is a plotting program and the bond-length bond-angle calculating program BONDLA, which can take useful results rapidly.

Table 3. Phases at the a) conventional method (classical methods at classical electrical furnaces at 860º K) b) non conventional method (microwave oven method at 60 minutes).

Chemical formula	Space group	z f.u./u.c	a (Å)	b (Å)	c (Å)	β°
Conventional method (classical methods at normal or classical furnaces at usally at 800° K)						
Ba_2PbCaO_6	Fm3m	4	8.5	8.6	8.6	
$BaCuO_2$	Im3m	90	18.2	18.3	18.3	
Ba_2PbO_4	I4/mmm	4	6.1	8.6	6.1	
CuO	C2/c	4	4.6	3.4	5.2	99.4
CaO	Fm3m	4	4.7	4.8	4.8	
2. Non Conventional methods (Microwave oven 60min)						
$Ba_{0.81}Ca_{0.19}CO_3$	Pmcn	4	5.3	8.8	6.5	
$BaPbO_3$	Imma	4	6.1	8.5	6.2	
CuO	C2/c	4	4.7	3.4	5.2	99.5

The refinement for each phase is solved out step-by-step, beginning always with the first phase, at the end of which the next defined phase was added, and so on up until the last one. At the first stages of crystal structure refinement we give an overall isotropic temperature factor and unitary populations, for all the atoms of the samples.

After the first stages some of the atom populations in the different phases were refined, step-by-step, keeping stable all the other factors while the final values of the atomic populations have assisted to calculate the correct chemical formula of crystal phases. So the chemical formula, the space group, the number z of formulae units per unit cell (f.u/u.c.), the unit cell parameters of the crystal phases, the R-factors (%) and the percentages of phases (% w/w) are given in table.

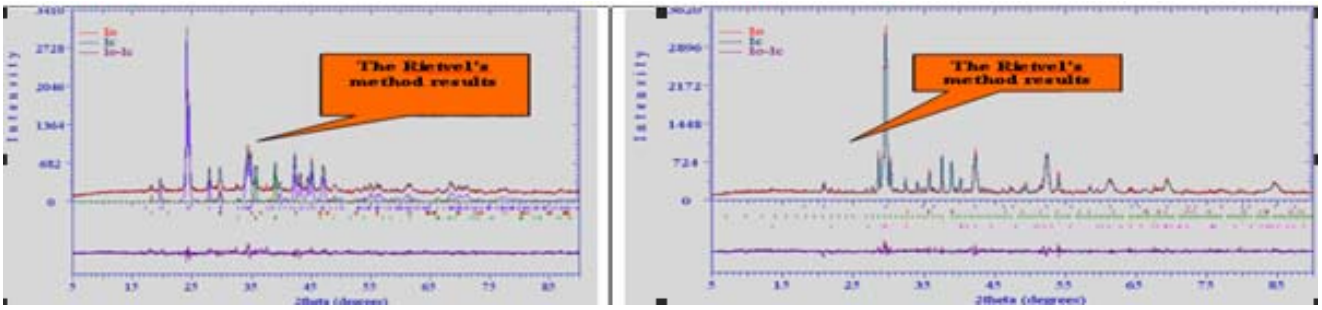

Fig. 6. Rietvel's analysis for the XRD measurements at 860 °K for the x=0.4 mixture for a) classical heating at 860 °K, b) microwave oven 800 Watt, 2.45 GHz and for 60 minutes.

4. Discussion and conclusions

CuO appears in every the sample and it means that is in excess from the beginning of the synthesis or it couldn't act because of an unknown factor. Increasing the pressure it is easy to obtain materials as polyoxides with one phase as it is mentioned in the Table 2, at pressures extremely high as 7GPa, 25GPa, 30GPa.

The discovery of existing of CaO in all the phases, tells that we have problem with the total absorbtion of this oxide from the final mixture.

The chemical reaction is deficient and probably is required more time, more heating, in order to have a fully understanding, or more pressure.

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