THE MICROWAVE EFFECTS ON THE COMPOUNDS SYNTHESIS OF Ba-Pb-Ca-Cu-O SYSTEM★

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A mixture corresponding to the general chemical formula $Ba_{(3-x)}Pb_xCa_2Cu_3O_{8+d}$ ($x = 0.2$), was prepared by suitable proportions of BaO, PbO, $CaCO_3$, CuO and heated by a microwave oven for 5min and next for 60min in free atmosphere. A second mixture with same chemical synthesis was prepared and heated by a conventional oven at 870°C, also in free atmosphere. The crystalline phases created in the three cases were studied by X-ray diffraction measurements and characterized, using the PDF2 database. Further, the Powder Profile Analysis (Rietveld's method) was used for the crystallographic study of the samples. Six phases were defined for the first sample, three for the second and five for third one. The results of the microwave oven method compared with the results of a conventional oven show interest differences. Analysis about the morphology of the samples and the concentrations of the elements took place by Scanning Electron Microscopy (SEM).

Key words: Superconductors, Crystal structure, Microwaves.

INTRODUCTION

The materials under study are a part of samples corresponding to a general starting chemical formula $Ba_{(3-x)}Pb_xCa_2Cu_3O_{8+d}$ (where $x = 0.2, \ldots, 1.0$). Usually, they are prepared from oxides or salts of component elements Ba, Pb, Ca, Cu, in suitable proportions, by heating in air, at high temperatures. In this work we have examined the crystalline compounds produced by two methods, by heating in a conventional electrical oven and by irradiation with a microwave oven. Some results about the chemical synthesis, with the method of microvave oven, were analysed in the case of the superconducting compound $YBa_2Cu_3O_7$, by D. R. Baghurstet *et al.* [1] and A. Agostino *et al.* [2]. Based on these facts, we have tried applications of this method for composing of our materials, which

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some times present inportant interesting, because exists a probability to show these high-Tc superconductivity.

COMPOSITION AND CHARACTERIZATION

In order to have a comparison of the two methods the two corresponding original mixtures were prepared by the same initial chemical proportions, in our laboratory, by mix of BaO, PbO, $CaCO_3$, and CuO, as starting materials, according to the general chemical formula:

$$(3\text{-}x)\text{BaO} + x\text{PbO} + 2\text{CaCO}_3 + 3\text{CuO} \rightarrow \text{Ba}_{(3-x)}\text{Pb}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+x}.$$

where $x = 0.2$. The first mixture was irradiated for 5 min, in air, up to red-hot, with a microwave oven, at a power level of 800 W and frequency 2.45 GHz and then was cooled to room temperature. To achieve a good homogenization, the sample was repowdered and reheated, for 60 min, in the same microwave oven, under the same conditions. Before and after the second 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 sample was prepared by heating of the second mixture in a conventional electrical furnace, at 870°C, for 36 h, was measured by the same X-Ray diffractometer, under the same conditions. The three XRD diagrams are given in Fig. 1.

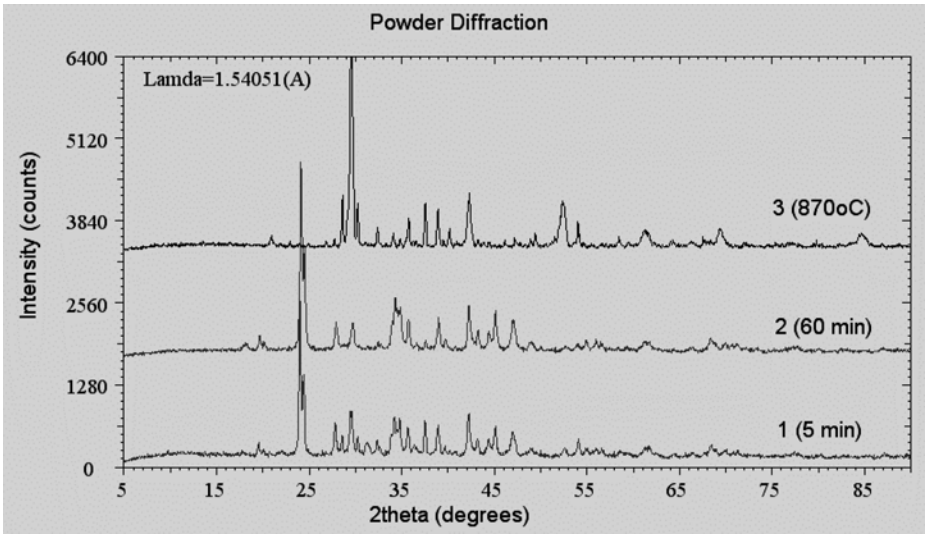

Fig. 1. – XRD diagrams (CuKα radiation) of samples produced by a microvave oven for 5 min [1], for 60 min [2] and at 870°C in a conventional electrical oven [3].

The powder XRD diagrams (Fig. 1) were plotted and studied by the program PLOTPOW [3]. As it is shown in this figure, the first two diagrams, 1 and 2, are similar, with light differences, located in some low peaks of first diagram, while the third diagram, appears very different from the first two diagrams. Using the program EVAWIN [4] and the PDF2 [5] database, the samples were characterized and the diagrams evaluated. Six phases were defined for the first sample ($BaCO_3$, CaO, CuO, $BaCuO_2$, $BaCu_2O_2$ and Ba_2CaPbO_6) [6–11], three for the second ($BaCO_3$, $BaPbO_3$ and CuO) [6, 12, 8] and five for the third one (Ba_2CaPbO_6, CuO, $BaCuO_2$, CaO and $BaPbO_3$) [11, 8, 9, 7, 12]. The main phases of the three samples are $BaCO_3$, $BaCO_3$ and Ba_2CaPbO_6, respectively. Detailed information about the defined phases is shown in Table 2.

SEM pictures of sample 1 and 3 (Fig. 2) show that most of the grains of first have a considerably smaller size than that obtained with a conventional oven. Moreover Fig. 2 shows the presence of voids in the microstructure, leading to low density material.

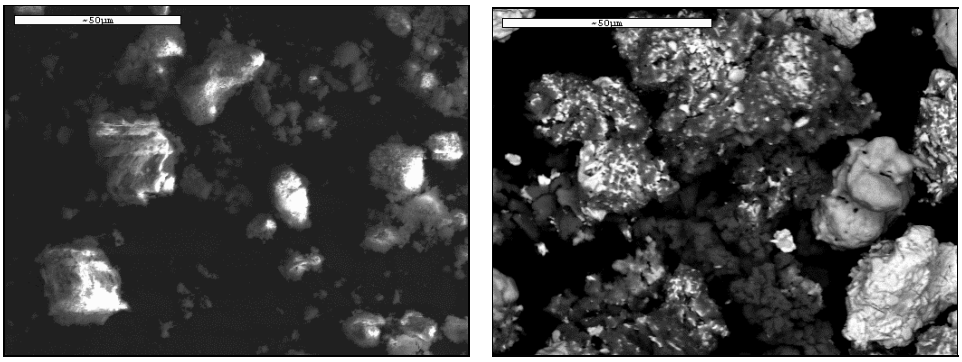

Fig. 2. – SEM images of sample 1 and 3 prepared as refered, by a microvave oven for 5min, and by a conventional oven.

STRUCTURE DETERMINATION AND REFINEMENT

Initial values of the crystal structure parameters (space group, unit cell parameters and atomic coordinates) of the phases, defined for all the samples, were taken from the bibliography and the ICSD [13] database. The refinement of the structure parameters was carried out by the program DBWSWIN [14], which is an edition of the program DBWS9411 [15] for Windows, based on the profile analysis (Rietveld's method) [16], improved and enhanced by a plotting program (DBWSPLOT) and a bond-length bond-angle calculating program (BONDLA), in order to take useful results directly.

The refinement for three cases carried out step-by-step, beginning with the first phase, at the end of which the next defined phase was added, and so on up

Table 2

Chemical formula, space group, number z of chemical units per unit cell, unit cell parameters of phases, R-factors (%) and percentages of phases (% w/w), after Rietveld refinement for the three cases

Chemical formula	Space group	z f.u./u.c	a [Å]	b [Å]	c [Å]	β°	% (w/w)
1. Microwave oven 5 min. R-p = 6.56%, R-wp = 8.37%, R-exp = 6.34%							
$Ba_{0.73}Ca_{0.27}CO_3$	Pmcn	4	5.2878	8.8693	6.4189		51.60
$BaCuO_2$	Im3m	90	18.2158	18.2158	18.2158		8.33
$BaCu_2O_2$	$I4_1/amd$	4	5.7113	5.7113	9.9512		6.53
Ba_2PbCaO_6	Fm3m	4	8.5325	8.5325	8.5325		3.80
CuO	C2/c	4	4.6765	3.4125	5.1123	99.53	14.71
CaO	Fm3m	4	4.7935	4.7935	4.7935		15.03
2. Microwave oven 60 min. R-p = 6.81%, R-wp = 8.85%, R-exp = 6.37%							
$Ba_{0.81}Ca_{0.19}CO_3$	Pmcn	4	5.3036	8.8995	6.4369		71.97
$BaPbO_3$	Imma	4	6.0735	8.5367	6.0139		5.98
CuO	C2/c	4	4.7002	3.4146	5.1309	99.52	22.04
3. Electrical oven 36 h. R-p = 7.66%, R-wp = 9.90%, R-exp = 6.88%							
Ba_2PbCaO_6	Fm3m	4	8.5688	8.5688	8.5688		51.23
$BaCuO_2$	Im3m	90	18.2857	18.2857	18.2857		18.63
Ba_2PbO_4	I4/mmm	4	6.0735	8.5367	6.0139		9.47
CuO	C2/c	4	4.6879	3.4139	5.1294	99.37	7.40
CaO	Fm3m	4	4.7935	4.7935	4.7935		13.26

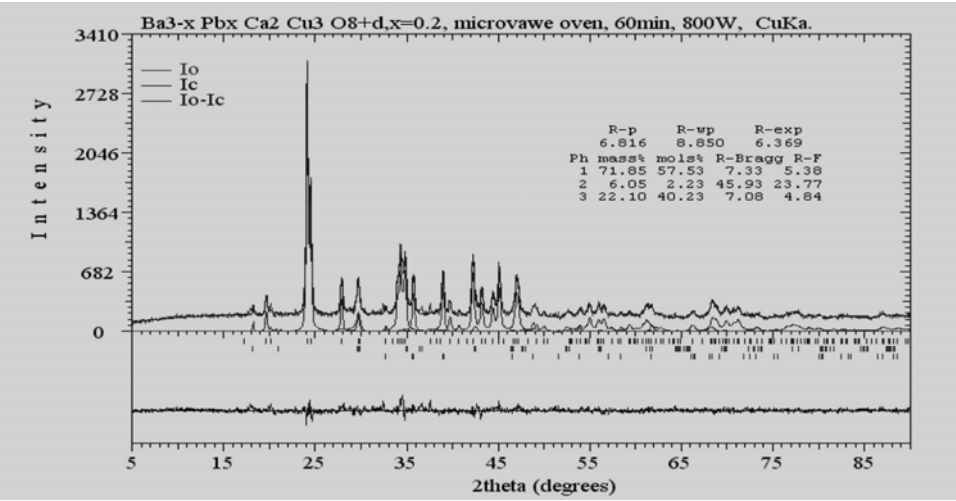

Fig. 3. – Results of the profile analysis with the Rietveld's method for the case 1 ($x = 0.2$), produced by a microwave oven for 5 min.

to last one. At first stages of the crystal structure refinement an overall isotropic temperature factor and unitary populations were used, for all atoms of the samples. In the next stages some of the atom populations in the different phases were refined, step-by-step, keeping stable all the other factors.

The final values of the atomic populations have assisted to calculate the correct chemical formula of crystal phases. 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 2.

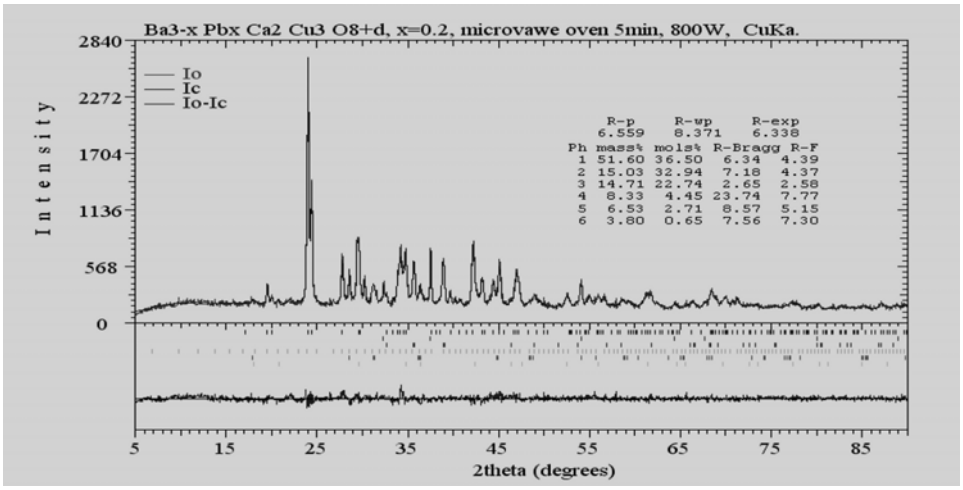

Fig. 4. – Results of the profile analysis with the Rietveld's method for the case 2 ($x = 0.2$).

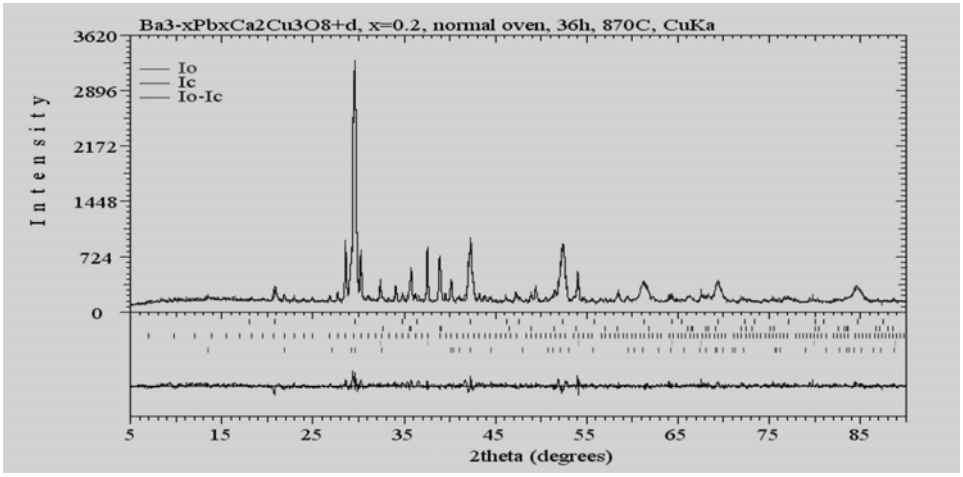

Fig. 5. – Results of the profile analysis with the Rietveld's method for the case 3 ($x = 0.2$), obtained by a conventional electrical oven for 36 h.

The results based on the diagrams 1, 2 and 3, after the refinement with the powder profile analysis (Rietveld's method), are plotted in Figs. 2, 3 and 4, where the diagrams of Io and Ic as functions of the 2θ angle are shown. The degree of agreement between the Io and Ic is shown with the transposed differential diagram of Io-Ic.

DISCUSSION

The characterization of the three samples and their refinement resulted totally in eight phases. As general result we can say is the impossibility of methods to synthesize a unique compound with starting proportions.

The existing of the CuO in whole of the samples means that is in excess from the beginning of the synthesis. From the number of phases is concluded that the case 2 is more successful than all remaining. The existing of CaO in cases 1 and 2 means that the chemical reaction is deficient and probably is required more time and more heating, respectively. Four out of eight phases ($BaCuO_2$, Ba_2PbCaO_6, CuO, CaO) are common in cases 1 and 3, that means the two methods like analogous. The compounds $Ba_{0.73}Ca_{0.27}CO_3$, $Ba_{0.81}Ca_{0.19}CO_3$ and Ba_2PbCaO_6 are the main phases for three cases, 1, 2 and 3 respectively, with percentages higher than 51%.

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