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Crystallographic study of component mixture getting $CeBa_2Cu_3O_y$

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A powder mixture of $BaCO_3$, Ce_2O_3 and CuO was prepared, according to the chemical formula $CeBa_2Cu_3O_y$. The mixture was annealed progressively, in free atmosphere, at temperatures 860°C to 940°C (with a step of 10°C) for 24 to 72h. Thus, nine samples were obtained and measured by X-Ray powder diffraction, at room temperature, by using a two-cycle diffractometer, with Bragg-Brentano geometry and CuKa radiation. Each sample was characterized with the help of the "Powder Diffraction File" (PDF). The initial crystal structure parameters of crystalline phases were taken from ICSD data base and refined, using the Rietveld's "Powder Profile Analysis". The refinement took place progressively, beginning with the powerful phase, at the end of which we added the next one and so on. Three phases were found for first sample: A=$BaCeO_3$ [Pm3m, a=4.3970(2)Å], B=CuO [C2/c, a=4.6902(2)Å, b=3.4163(8)Å, c=5.129(2)Å, β=99.39°(2)] and C=$BaCuO_2$ [Im3m, a=18.288(1)Å]. For the remaining samples the phases A and B were found [for last sample Pm3m, a=4.3595(3)Å and C2/c, a=4.6917(7)Å, b=3.4191(6)Å, c=5.1291(7)Å, β=99.58°(1), respectively]. The C phase appears only in the first sample. The phase A was the main phase and its percentages for the different temperatures are altered between 55.9% and 82.8% w/w, while of B phase between 12.1% and 30.7%. The percentage of C phase is about of 32.05% w/w.

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Keywords: Superconductivity, Crystal structure, Phase characterization, Rietveld's method

1. Introduction

In this paper, the under study materials, constitute a part of a series of oxides created from mixtures of salts or oxides of component elements Ba, Rare Earth, Cu by heating in air, at high temperatures (higher than 850°C). The first aim of this work was the exactly study of the conditions under of which the crystalline phases are created and mainly these that present high Tc superconductivity, known that, materials with crystal structure analogous to the compound $YBa_2Cu_{2.862}O_{6.62}$ [1] present high Tc superconductivity ($YBa_2Cu_3O_{6.62}$) [2]. On the other hand, while the mixed oxides of rare earths with Ba and Cu [$(Sm,Ba,Ce)_8Cu_6O_z$, $(Nd,Ba,Sr,Ce)_8Cu_6O_z$, $(La,Gd,Ba,Ce)_8Cu_6O_z$ and $(La,Gd,Ba,Sr,Ce)_8$ Cu_6Oz] are superconductors [3], the orthorhombic $(Gd, Ce)_4(La, Ba)_4Cu_6O_{17.94}$ is nonsuperconductor [4]. Additionally, the structural properties of these produced compounds and the variation of the crystal phase percentages in the samples were studied.

2. Composition

Table 1. Molecular weights, proportions, percentages and weight (gr) of the initial components that were used for a 2 gr sample of $CeBa_2Cu_3O_y$.

Compound	Molecular weight	Mult.	%	Weight (gr)
$BaCO_3$	197.3480	2	49.49	0.9899
Ce_2O_3	328.2382	0.5	20.58	0.4116
CuO	79.5450	3	29.92	0.5985

A mixture of 2 gr was prepared by mixing of oxides $BaCO_3$, Ce_2O_3 and CuO in proportions 2: 1/2: 3, according to chemical equation:

$$0.5\cdot Ce_2O_3+2\cdot BaCO_3+3\cdot CuO \rightarrow CeBa_2Cu_3O_y.$$

The proportions and the percentages that were used for each substance are shown in Table 1.

The mixture was heated for several hours (24 to 72h) at temperatures from 860 °C up to 910 °C with a step of 10 °C and was cooled progressively at room temperature. Thus nine samples (1 to 9, corresponded to temperatures 860 °C to 910 °C) were obtained and examined.

3. Characterization

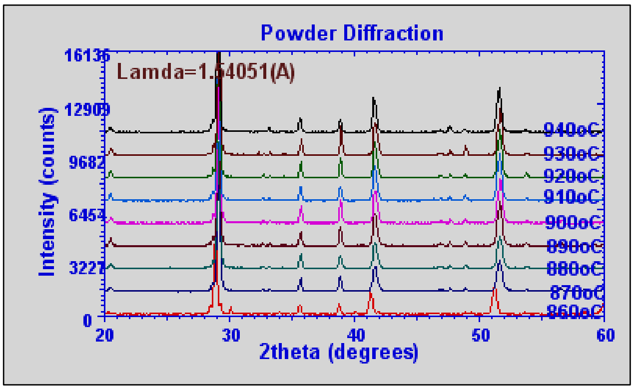


Fig. 1. XRD diagrams of the all the samples.

For each of the nine samples, prepared after heating at the corresponding temperature and cooling at the room temperature, XRD diagrams were obtained, by a two-circle diffractometer with Bragg-Brentano geometry [5] and CuKa radiation. The scan took place in 2θ angles between 5° and 90° with a step-scan of 0.05° and a scan-time 5 sec. The XRD diagrams were studied and investigated with the program PLOTPOW [6]. The existing phases in the samples were defined with the program EVAWIN [7], which uses the PDF2 database [8]. The nine XRD diagrams of samples are given in Fig. 1.

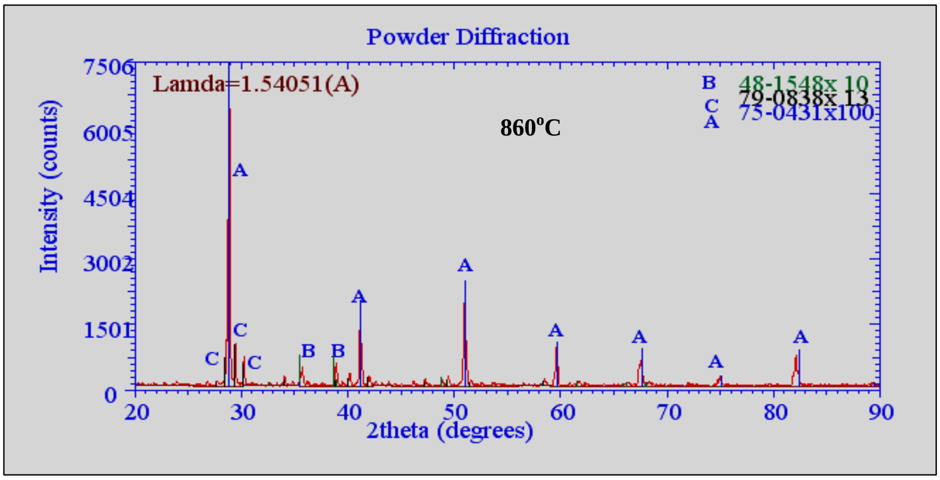


Fig. 2. Characterization of first sample (860°C) by EVAWIN.

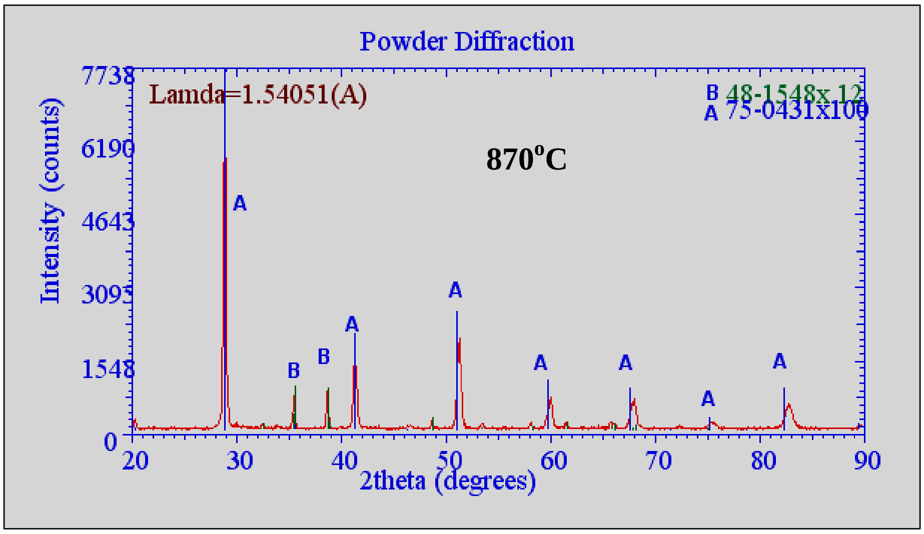


Fig. 3. Characterization of second sample (870°C) by EVAWIN.

In the first sample (860 ^{O}C) three phases were determined: A=BaCeO$_3$ [9], [10], B=CuO [11] and C=BaCuO$_2$ [12] (Fig. 2). In the next samples, obtained in temperatures higher than 860^{O}C, only the first two phases exist (Fig. 3, 4), while the C phase disappears. Thus only two phases there are in the eight samples prepared at 870°C to 940°C. As it is shown in the Fig. 1, the two characteristic peaks of B phase appear at 35.5^{O} and 38.7^{O}, while the characteristic three peaks of C phase are shown between 28° and 30.5°. All the remaining strong peaks, found at 2θ angles 20.5°, 29.1°, 41.5°, 51.1°, 60.2°, 68.2°, 75.6° and 83.1°, belong to A phase (BaCeO$_3$). The phase A was the main phase and its percentages for the different temperatures are altered between 55.9 and 82.8% w/w, while of B phase between 12.1 and 30.7%. The percentage of C phase, existing only in the first sample, is 32.0% w/w. The minimum value of percentage of A phase was presented at temperature of 860 ^{O}C, while the maximum at 920 ^{O}C.

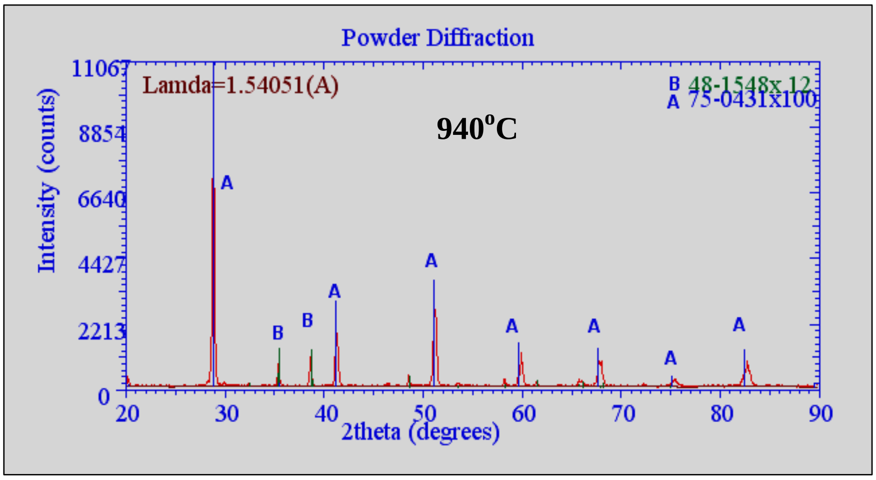
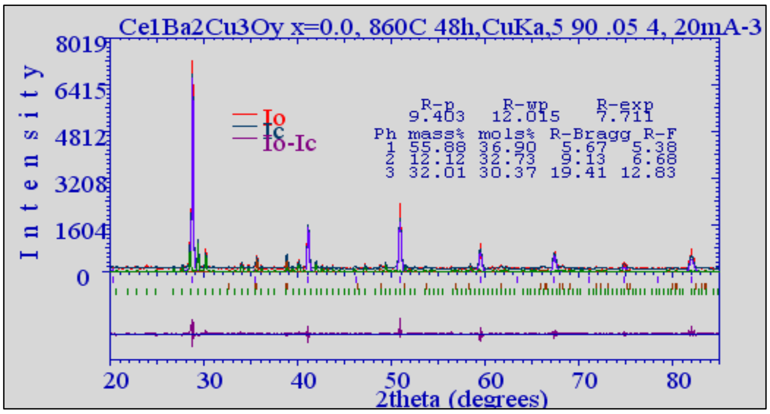


Fig. 4. Characterization of last sample (940°C) by EVAWIN.

4. Crystal structure refinement

After the characterization of the samples with PDF data-base, initial crystal structure parameters (space group, unit cell constants and atomic coordinates) of defined crystalline phases were taken from ICSD data-base and refined, using the Rietveld's method (Powder Profile Analysis).



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  R-p      R-wp     R-exp
 9.403   12.015    7.711
Ph mass% mols% R-Bragg R-F
 1 55.88 36.90  5.67   5.38
 2 12.12 32.73  9.13   6.68
 3 32.01 30.37 19.41  12.83
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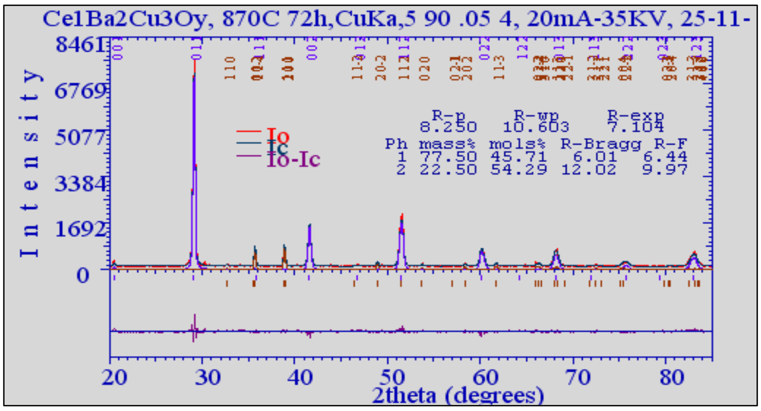
Fig. 5. Results of Rietveld analysis for the first sample (860^{O}C).



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  R-p      R-wp     R-exp
 8.250   10.603    7.104
Ph mass% mols% R-Bragg R-F
 1 77.50 45.71  6.01   6.44
 2 22.50 54.29 12.02   9.97
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Fig. 6. Results of Rietveld analysis for the sample (870^{O}C).

Refinement of the structure parameters of the three phases was achieved with the Rietveld method [13] applying the program DBWSWIN [14]. The refinement took place step-by-step for each phase and finally for all together. In all the steps an isotropic temperature factor was used. In some cases, where it was essential, the atomic site occupation factors were refined. The values of residual index Rp fluctuate between 0.081 (sample 4) and 10.5 (sample 8). The high value of residual index for the sample 8 is owed in the primely high value of the peak at $2\theta=49^o$.

The heating duration, the space groups, the unit cell constants and their standard deviations of all phases are given in Table 2. The percentages of phases and the R-factors in each temperature are given in Table 3.

The results of refinement with the Rietveld analysis for three of the nine samples (860 °C, 870 °C, 940 °C) are presented in the Figs. 2, 3 and 4. The non presented samples (880 °C, 890 °C, 930 °C) present inappreciable changes and for this reason were omitted. In these figures, the diagrams of intensities Io and Ic (observed and calculated) as a interrelation of 2θ are shown. The degree of agreement between Io and Ic is given in the lower part of the figures with a diagram that shows the change I_o-Ic. The positions of reflections of various phases are presented in the down part of figures with small colourful lines. Also, in the same diagrams are presented the percentages of phases and the R-factors of refinement. The profile of each phase is presented analytically with different color in the Figs. 5, 6 and 7, while the Miller indices of reflections are shown on the upper place of the Fig. 6 and 7 for the samples of 870 °C and 940 °C.

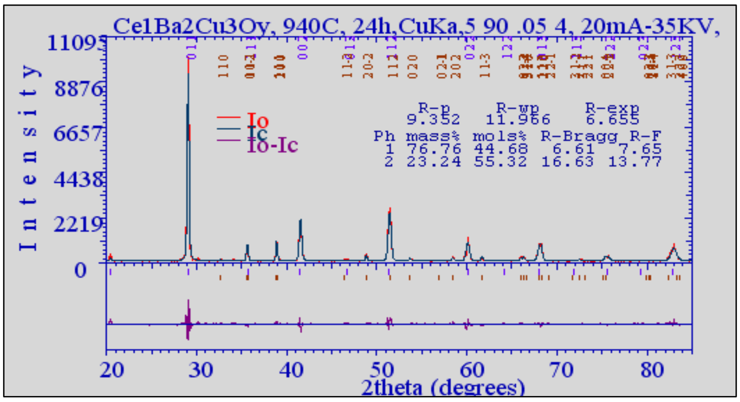

Fig. 7. Results of Rietveld analysis for the sample (940^{O}C).

Table 2. Heating temperatures and duration, phase names, space groups and unit cell constants of all phases as they resulted from the Rietveld analysis. (A = $BaCeO_3$, B=CuO, C=$BaCuO_2$).

Sample	T (°C)	Time (h)	Phase	Space Group	a Å	b Å	c Å	B°
1	860	75	A	Pm3m	4.397(2)			
			B	C2/c	4.6920(8)	3.417(1)	5.131(1)	99.41(2)
			C	Im3m	18.289(1)			
2	870	64	A	Pm3m	4.3570(3)			
			B	C2/c	4.6921(9)	3.4197(5)	5.1314(8)	99.39(1)
3	880	56	A	Pm3m	4.3561(3)			
			B	C2/c	4.6914(9)	3.4187(6)	5.1318(9)	99.46(1)
4	890	72	A	Pm3m	4.3566(2)			
			B	C2/c	4.6904(8)	3.4191(6)	5.1322(9)	99.48(1)
5	900	52	A	Pm3m	4.3576(2)			
			B	C2/c	4.6927(8)	3.4222(3)	5.1327(9)	99.55(1)
6	910	74	A	Pm3m	4.3573(3)			
			B	C2/c	4.6933(8)	3.4164(5)	5.1318(8)	99.50(1)
7	920	48	A	Pm3m	4.3606(3)			
			B	C2/c	4.6965(8)	3.4188(6)	5.1358(9)	99.51(1)
8	930	48	A	Pm3m	4.3585(4)			
			B	C2/c	4.6960(1)	3.4182(6)	5.129(1)	99.57(1)
9	940	48	A	Pm3m	4.3595(3)			
			B	C2/c	4.6917(7)	3.4191(5)	5.1320(7)	99.58(1)

5. Analysis of the structures and discussion

The characterization of the nine samples and their refinement resulted in total in three phases (A=$BaCeO_3$, B=CuO, C=$BaCuO_2$). All these exist in the sample 1. The phases A and B exist in all the samples. As it is shown in Table 3, the first phase (A) is the main phase, presenting an increase of its percentage from 55.9% to 82.8 %, for the samples 1 to 9. Its minimum percentage corresponds to temperature of 860 °C and the maximum to 920 °C. The pecentage of the B phase fluctuates between 12.1% (860 °C) and 30.7% (910 °C). The phase C exists with a percentage of 32% only in the sample 1 and disappears in the next samples. The A phase is encouraged in temperatures higher than 860 °C; on the contrary with the C phase that is encouraged in lower. The initial component CuO (phase B) partially reacts with the Ba compound only in the first sample and gives the C phase. In the remaining samples no one reaction does take place between this and the other components. The quantity of Ce exists only in phase A, which exists in all the samples. In the next the structure of the main phase is examined briefly.

Table 3. Percentages of phases A=$BaCeO_3$, B=CuO, C=$BaCuO_2$ and residual indices in the samples, after the Rietveld analysis.

Sample	T(°C)	A	B	C	Rp	Rwp	Rexp
1	860	55.9	12.1	32.0	9.4	12.0	7.7
2	870	77.5	22.5	-	8.2	10.6	7.1
3	880	80.8	19.2	-	8.7	11.4	6.9
4	890	80.3	19.7	-	8.1	10.6	6.8
5	900	75.8	24.2	-	8.9	11.5	6.6
6	910	69.3	30.7	-	9.5	12.2	6.5
7	920	82.8	17.2	-	9.6	12.4	6.9
8	930	79.7	20.3	-	10.5	13.7	6.5
9	940	76.8	23.2	-	9.3	11.9	6.6

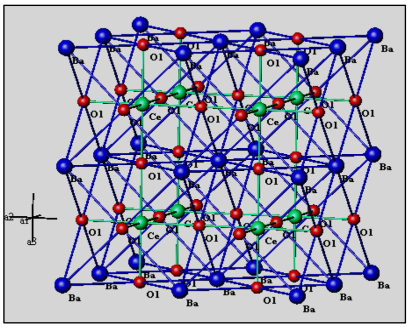

Fig. 8. Crystal structure of A phase ($BaCeO_3$). Ba=blue spheres, Ce=green spheres and O=red spheres.

As it is sown in the structure of the main phase (Fig. 8), there are two types of successive layers, parallel the plane (a,b). The first one is constituted by Ba and O atoms while the second by Ce and O atms. The Ba atoms are twelve coordinated by twelve oxygen atoms found at three layers and in the same distances of 3.081Å. The four of the oxygen atoms are in the same plane with the Ba atoms and the remaning eight (4+4) are on the two Ce-O planes, from both sides of the Ba-O plane. The Ce atoms are six coordinated by six oxygen atoms, forming normal octahedra with distances Ce-O=2.178(Å). Four of oxygen atoms lie on the Ce-O leyer and the other two (1+1) on the two Ba-O planes from both sides of the Ce-O plane.

Analogous structures have the compounds $BaCeO_3$, $BaZrO_3$, $BaSnO_3$ [15] and $BaCe_xZr_{1-x}O_3$ [16]. The remaining phase structures (B and C), as defined after refinement, are in accordance with those reported in bibliography, with some slight variations, but without any interesting.

6. Conclusions

In this work an effort was made to prepare an oxide containing Ba-Ce-Cu-O. From the phases $BaCeO_3$, CuO and $BaCuO_2$ that found no one does satisfy our wish. This means that the conditions in the range of temperatures 860 °C to 940 °C do not encourage the reaction to form a compound with these elements. Despite these however were extrapolated useful conclusions related with the behavior of these elements in the mentioned range of temperatures and with the crystal structures of products obtained by this thermal chemical reaction.

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