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Crystallographic study of $Nd_xBa_{1-x}CuO_y$ (x=0.2, 0.4, 0.6, 0.8) compounds prepared by heating of component mixtures

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Four powder mixtures of $BaCO_3$, Nd_2O_3 and CuO was prepared according to the general chemical formula $Nd_xBa_{1-x}CuO_y$, where x=0.2, 0.4, 0.6, 0.8. The mixtures were heated for 65h in free atmosphere at temperature 930°C. The products were cooled at room temperature and measured by an X-Ray powder diffractometer with Bragg-Brentano geometry and CuKα radiation. Each of the samples was characterized with the help of the "Powder Diffraction File" (PDF). The initial crystal structure parameters of found crystalline phases were taken from ICSD data-base and refined, using the Rietveld's method. Constant temperature factors for all atoms were used. Four phases were found for whole of the samples: A=$NdBa_2Cu_3O_{6.6}$ (Pmmm, a=3.883 to 3.912Å, b=3.843 to 3.889Å, c=11.576 to 11.725Å), B=$BaCuO_2$ (Im3m, a=18.301Å), C=Nd_2CuO_4 (I4/mmm, a=3.943Å, c=12.173Å), and D=CuO (a=4.794Å, b=3.362Å, c=5.228Å, β=99.79°). The phase A is the main phase and exists in all the samples. In the first sample (x=0.2) the phases A and B were found with percentages 76.8% and 23.2%. In the samples 2 and 3 (x=0.4 and x=0.6) only the A phase exists, while in the fourth one the A, C and D phases exist, with percentages 48.9%, 37.4% and 13.7%.

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Keywords: Crystal growth, Crystal structure, Superconductivity, 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 tetragonal single crystals $YBa_2Cu_{2.862}O_{6.62}$ [1] present high Tc superconductivity, with Tc ≈ 50 K. ($YBa_2Cu_3O_{6.62}$) [2]. Also 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], while the orthorhombic $(Gd, Ce)_4(La, Ba)_4Cu_6O_{17.94}$ is nonsuperconductor [4]. Additionally, the structural properties of these produced compounds and the percentage variation of the crystal phases in the different samples were studied.

2. Experimental

Four powder mixtures of compounds $BaCO_3$, Nd_2O_3 and CuO were prepared, according to the chemical formula:

$(x/2)Nd_2O_3+(1-x)BaCO_3+CuO \rightarrow Nd_xBa_{1-x}CuO_y$, where x=0.2, 0.4, 0.6, 0.8.

The mixtures were heated for 65h in free atmosphere at temperature 930°C and then were progressively cooled at room temperature products. Thus, four black color samples, 1, 2, 3 and 4, with initial synthesis:

$Nd_{0.2}Ba_{0.8}CuO_y$, $Nd_{0.4}Ba_{0.6}CuO_y$, $Nd_{0.6}Ba_{0.4}CuO_y$ and $Nd_{0.8}Ba_{0.2}CuO_y$

were taken.The obtained samples were pulverized and examined by X-ray techniques, using an automated X-Ray powder diffractometer (Philips 1050), with Bragg-Brentano geometry (θ-2θ) [5] and CuKα radiation. The scan took place in 2θ angles between 5° and 90° with a step-scan of 0.05° and a scan-time 5sec.

3. Characterization

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]. As we can see in Fig. 1, from the investigation and evaluation the of four XRD diagrams, for the first sample (x=0.2) two phases were determined: A=$NdBa_2Cu_3O_{6.6}$ (Pmmm, a=3.883Å, b=3.843Å, c=11.576Å) [9], B=$BaCuO_2$ (Im3m, a=18.3Å)

[10] (figure 2). In the next two samples 2 and 3 (x=0.4, 0.6), only the phase (A) exists (figures 3, 4), while in the fourth sample (x=0.8) exists also the phase A and two new phases C=Nd_2CuO_4 (I4/mmm, a=3.943Å, c=12.173Å) [11] and D=CuO (a=4.794Å, b=3.362Å, c=5.228Å, β=99.79°) [12].

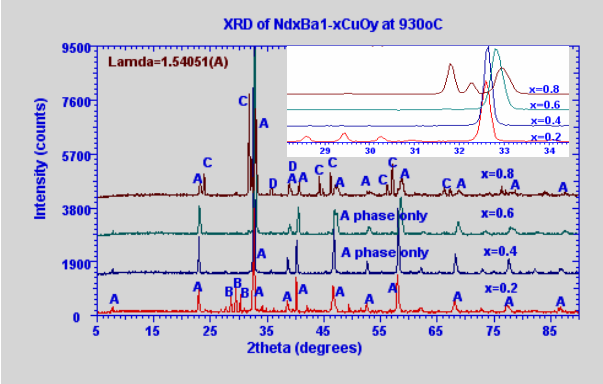

Fig. 1. XRD diagrams: Comparison and phase characterization.

The maximum peak of phase A is shifted at right-hand, as the quantity x of Nd increases, from 32.6° for x=0.2 to 33° for x=0.8 (figure 1). Due to this shifting of the peaks is expected a miniaturization of the unit cell by miniaturization of its parameters, a, b, c. This shifting is better shown in the inset small figure of figure 1, which represents in detailed the region 28 to 34 degrees. As it is shown in this figure for the sample 1 in the region 28° to 31° there are three peaks characteristic of phase B. In the same figure for x=0.8 (sample 4) appear three new strong peaks at the region of 31.4° to 33.3°, which characterize the phase C. Also in the region 35° to 39° of figure 1 for the sample 4, there are two small peaks which characterize the phase D.

Thus, for x=0.2 appear two phases A and B, while for x=0.4 and x=0.6 appears only the phase A (single phase samples). More for x=0.8 appear two phases, A and C, and remains an excess of CuO as third phase.

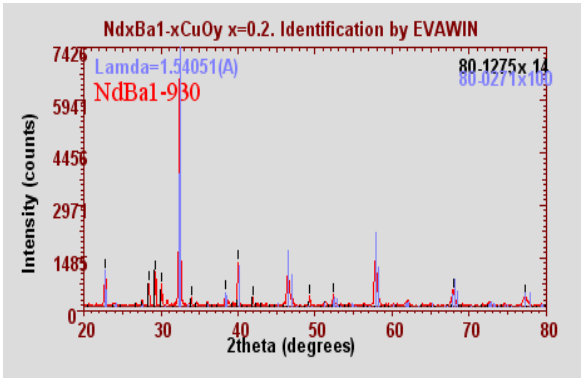

Fig. 2. XRD of sample 1and identification of phases A and B.

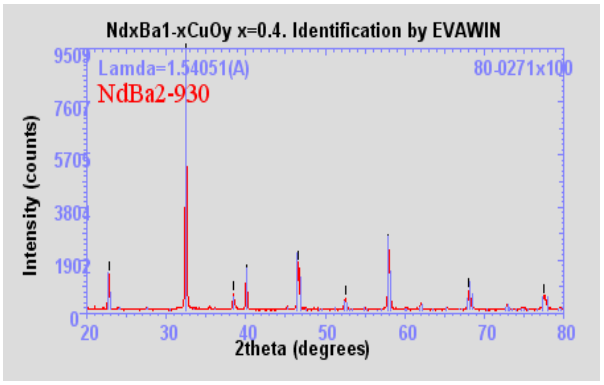

Fig. 3. XRD of sample 2 and identification of phase A.

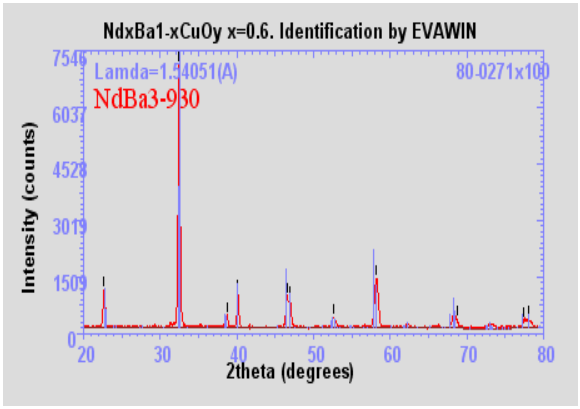

Fig. 4. XRD of sample 3 and identification of phase A.

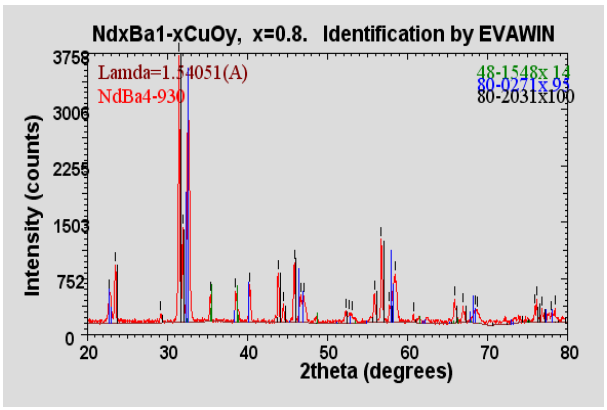

Fig. 5. XRD of sample 4 and identification of phases A, C and D.

4. Crystal structure refinement

After the characterization of the samples, 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) [13], applying the program DBWSWIN [14]. The refinement was realized 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 6.77% (sample 4) and 7.75% (sample 3). The space groups, the unit cell constants and their standard deviations of all phases are given in the Table 1. The percentages of phases and the R-factors for all the samples are given in table 2. The final atomic coordinates and their standard deviations in parenthesis are given in the Table 3. The interatomic distances between the central cations and neighbouring oxygen atoms, which form the corresponding coordination polyhedra, are given in the Table 4.

Table 1. Space groups, unit cell parameters and their standard deviations of all phases.

Sample	x	Phase	Space Group	a	b	c	β
1	0.2	A	Pmmm	3.9123(5)	3.8893(3)	11.725(2)	
		B	Im3m	18.3012(13)			
2	0.4	A	Pmmm	3.8918(3)	3.8862(3)	11.698(1)	
3	0.6	A	Pmmm	3.8836(4)	3.8482(5)	11.582(2)	
4	0.8	A	Pmmm	3.8831(5)	3.8433(7)	11.576(2)	
		C	I4/mmm	3.9431(2)		12.1726(8)	
		D	C2/c	4.794(3)	3.362(1)	5.228(2)	99.79(4)

Table 2. Percentages of phases and residual indices for all samples, after the Rietveld analysis.

Sample	x	A	B	C	D	Rp	Rwp	Rexp
1	0.2	76.84	23.16	-	-	7.71	10.06	7.03
2	0.4	100	-	-	-	7.44	9.75	6.96
3	0.6	100	-	-	-	7.75	10.12	6..45
4	0.8	48.86	-	37.44	13.69	6.77	8.69	6.40

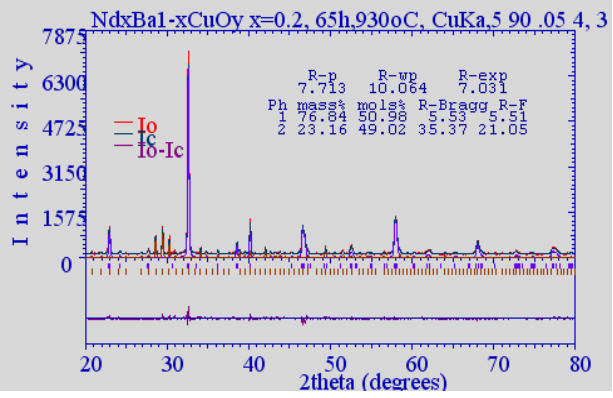

Fig. 6. Results of Rietveld analysis for the first sample (x=0.2).

Table 3. Atomic coordinates and their standard deviations for four phases A, B, C and D, after Rietveld refinement.

Phase A ($NdBa_2Cu_3O_{6.6}$)			
atom	x	y	z
Nd	1/2	1/2	1/2
Ba	1/2	1/2	0.1836(4)
Cu1	0	0	0
Cu2	0	0	0.3506(9)
O1	0	1/2	0
O2	1/2	0	0.372(5)
O3	0	1/2	0.371(5)
O4	0	0	0.154(4)
O5	1/2	0	0
Phase B ($BaCuO_2$)			
atom	x	y	z
Ba1	0	0.1510(9)	0.3100(8)
Ba2	0	0.3640(8)	0.3640(8)
Ba3	0.1770(9)	0.1770(9)	0.1770(9)
Cu1	1/4	0.150(1)	0.350(1)
Cu2	0	0.125(2)	0.125(2)
Cu3	0.206(3)	0	0
Cu4	0.430(7)	0	0
O1	0.072(5)	0.072(5)	0.186(5)
O2	0.144(4)	0.144(4)	0.343(7)
O3	0.267(5)	0.267(5)	0.085(8)
O4	1/4	0	1/2
O5	0.318(15)	0	0
O6	0	0.112(22)	0.440(21)
Phase C (Nd_2CuO_4)			
atom	x	y	z
Nd	0	0	0.3513(3)
Cu	0	0	0
O1	0	1/2	0
O2	0	1/2	1/4
Phase D (CuO)			
atom	x	y	z
Cu	1/4	1/4	0
O1	0	0.476(13)	1/4

The results of refinement with the Rietveld analysis for all the samples (x=0.2, 0.4, 0.6, 0.8) are presented in the Figs. 6, 7, 8 and 9. In these figures, the diagrams of intensities Io and Ic (observed and calculated) as an interrelation of 2θ are shown. The degree of agreement between Io and Ic is given at 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 figures 6, 7, 8, and 9, while the Miller indices of reflections are

shown on the upper place of the Figs. 7 and 8 for the single phase samples 2 and 3.

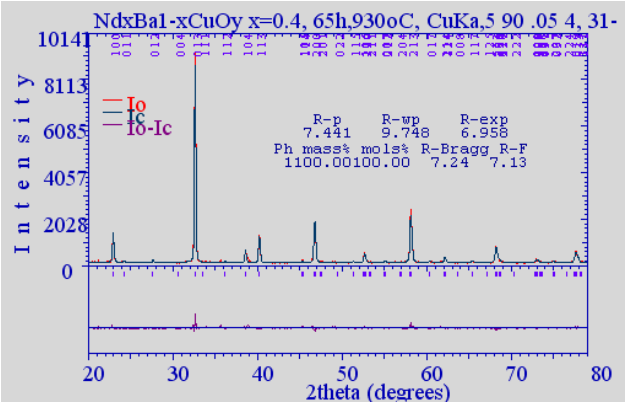

Fig. 7. Results of Rietveld analysis for the second sample (x=0.4).

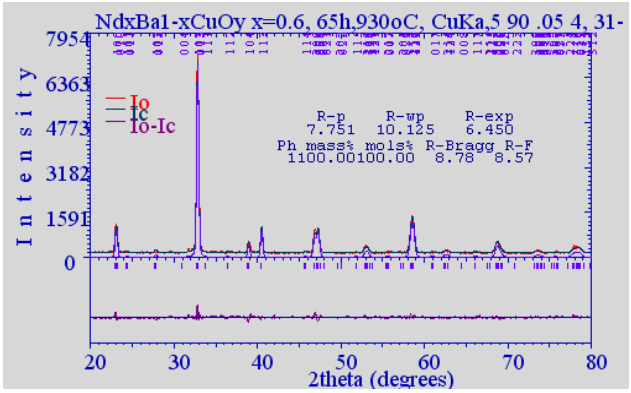

Fig. 8. Results of Rietveld analysis for the third sample (x=0.6).

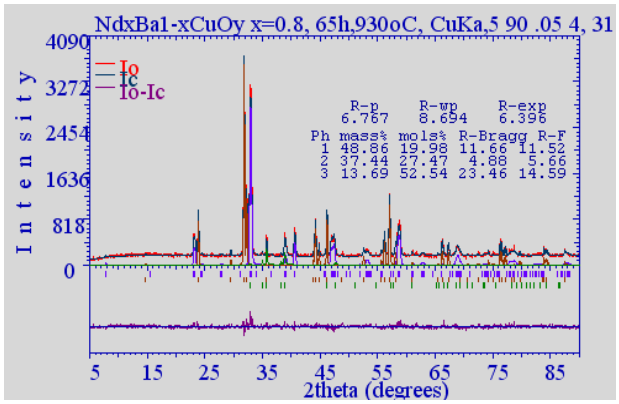

Fig. 9. Results of Rietveld analysis for the fourth sample (x=0.8).

Table 4. Interatomic distances (Å) between cations and oxygen atoms of four phases A, B, C and D.

Phase A ($NdBa_2Cu_3O_{6.6}$)	
Nd - O2x4	2.43(3)
O3x4	2.45(3)
Ba - O4x4	2.755(6)
O5x2	2.867(3)
O1x2	2.879(3)
O2x2	2.91(4)
O3x2	2.92(4)
Cu1-O4x2	1.79(4)
O1x2	1.924
O5x2	1.942
Cu2-O3x2	1.939(7)
O2x2	1.957(7)
O4x1	2.27(4)
Phase B ($BaCuO_2$)	
Ba1-O6x1	2.48(15)
O2x2	2.71(8)
O3x2	2.75(9)
O5x1	2.77(2)
O1x2	2.99(9)
Ba2-O6x4	2.76(12)
O2x2	2.88(8)
O3x2	2.95(10)
O4x2	3.25(1)
Ba3-O1x3	2.72(9)
O3x3	2.87(10)
O2x3	3.16(8)
Cu1-O2x2	1.95(8)
O3x2	1.95(10)
Cu2-O1x4	1.98(9)
Cu3-O1x4	1.90(9)
O5x1	2.05(15)
Cu4-Ox4	2.04(12)
Ox1	2.05(11)
Phase C (Nd_2CuO_4)	
Nd –O2x4	2.326(2)
O1x4	2.676(2)
Cu –O1x4	1.972
Phase D (CuO)	
Cu –O1x2	1.86(2)
O2x2	2.06(1)

4. Analysis of the structures and discussion

The characterization of the four samples and their refinement resulted totally in four phases (A=$NdBa_2Cu_3O_{6.57}$, B=$BaCuO_2$, C=Nd_2CuO_4, D=CuO). The phase A exists in all the samples and the phase B exists only in the sample 1. The phases C and D exist only in the sample 4. The samples 2 and 3 consist only from the phase A.

Taking into consideration the results of phase identification, the initial constitution of the samples and the results of refinement, as these obtained by the method of Rietveld, we are led to the following likely chemical reactions for the four samples:

Sample1, x=0.2: $4Nd_{0.2}Ba_{0.8}CuO_4 \rightarrow (Nd_{0.8}Ba_{0.2})Ba_2Cu_3O_{6.4} + BaCuO_2$.

Sample2, x=0.4: $3Nd_{0.4}Ba_{0.6}CuO_4 \rightarrow Nd(Ba_{1.8}Nd_{0.2})Cu_3O_{6.6}$.

Sample3, x=0.6: $3Nd_{0.6}Ba_{0.4}CuO_4 \rightarrow Nd(Ba_{1.2}Nd_{0.8})Cu_3O_{6.9}$.

Sample4, x=0.8: $5Nd_{0.8}Ba_{0.2}CuO_4 \rightarrow Nd(BaNd)Cu_3O_7 + Nd_2CuO_4 + CuO$.

As the products have described, we can conclude that the Nd and Ba atoms are distributed in two crystallographic sites of phase A, namely 1h and 2t of space group Pmmm. The distribution depends on the quantity x of Nd and the 1-x of Ba. Thus in the first sample, since the quantity x is small, the first site (1h) is partialy occupied by both Ba and Nd atoms, while the second is occupied only by Ba. In the remaining samples the quantity of Nd appears in excess for sites 1h. Thus, these sites are full occupied by Nd and the excess of this accomplishes the second sites 2t together with the Ba.

As it is shown in Table 2, the phase A is the main phase. Its percentage increases from 76.84% for x=0.2 to 100 % for x=0.4 and x=0.6 and then decreases to 48.86% for x=0.8. The percentage of the B phase is 23.16%, while of C and D are 37.44% and 13.69% respectivelly. For x=0.8 the initial component CuO reacts partially with the initial compounds of $BaCO_3$ and Nd_2O_3 giving the phases A and C, while the non reacted quantity appears as phase D in the final products. That means the CuO is in excess for x=0.8.

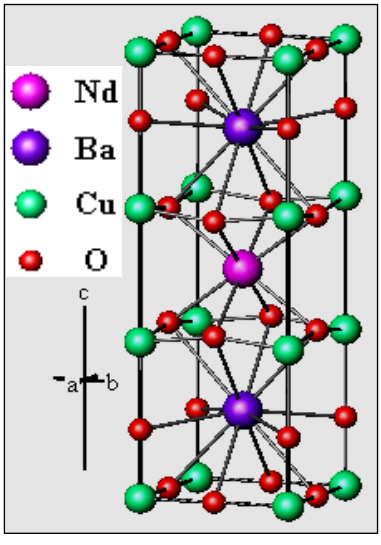

Fig. 10. Unit cell of phase A=$NdBa_2Cu_3O_{6.57}$.

In the next paragraphs, the structures of the found phases are briefly examined.

As it is shown in the structure of **the phase A** (Fig. 10), the atoms of Nd lie on a layer parallel to a,b with z=1/2. Each of Nd atoms is surrounded by eight oxygen atoms forming an erect tetragonal prism. The eight oxygen atoms lie on the two mixed atom layers, the Cu-O layers, four of which are at z=0.37 and the other four at z=0.63.

The Ba atoms lie on two mixed Ba-O layers with z=0.19 and 0.81, from both sides of Nd layers in distances of 3.69 Å from these. Each of the Ba atoms is surrounded by 12 oxygen atoms forming a polyhedron with 18 faces of which the two tetragonal bases are parallel to plane of (a, b), while the adjacent surface, recommended from two groups of 8 triangular faces, are about symmetrical each to other by a mirror plane, identified with Ba-O layer. Four of O atoms lie on the first mixed Cu-O layer (z=0) and other four on the second Cu-O layer (z=0.37). The remaining four oxygen atoms lie on the intermediate mixed Ba-O layer with z=0.15.

More, there are two types of Cu atoms, Cu1 with z=0 and Cu2 with z=0.35, lying on the corresponding mixed Cu-O layers. The first of these is six coordinated by six O atoms, forming a tetragonal dipyramid. Four of these O atoms lie on the same plane with the Cu1 atom, forming the tetragonal base, while the other two from both sides of the Cu-O plane.

The second type of Cu is five coordinated by five O atoms, forming a tetragonal pyramid. Four of the O atoms with z=0.37 lie almost on the same plane with the Cu2 atom, forming about a square, the center of which is occupied by the Cu atom. The fifth one is in a larger distance on the perpendicular to plane direction passed by Cu2 atom.

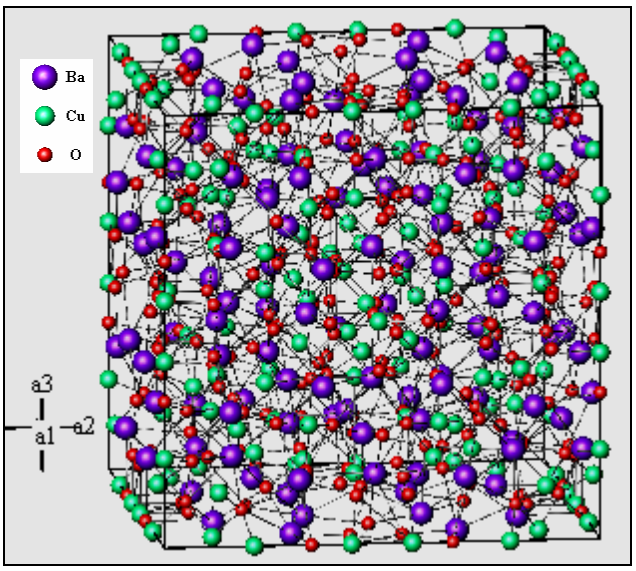

Fig. 11. Unit cell of phase B=$BaCuO_2$

In the phase B (Fig. 11) the Ba atoms are in the three sites Ba1, Ba2, Ba3, with different coordination. From

these the Ba1 atom is eight-coordinated by seven oxygen atoms in distances 2.71Å to 2.76Å and an other in 3.00Å. The Ba2 atom is ten-coordinated by eight oxygen atoms in distances 2.76Å to 2.95Å and an other pair in 3.25Å. The Ba3 atom is nine-coordinated by six oxygen atoms in distances 2.72Å to 2.87Å and three other in 3.16Å

The Cu atoms are in three sites Cu1, Cu2, Cu3 and Cu4. The first two are with tetragonal coordination and distances Cu-O between 1.947 Å and 1.954 Å for Cu1 and 1.981 Å for Cu2. The remaining Cu atoms, Cu3 and Cu4, are five coordinated by four oxygen atoms in tetragonal coordination, in distances 1.899Å for Cu3 and 2.058 Å for Cu4, and an oxygen in the apex of formed tetragonal pyramid, in distance 2.050 Å for both Cu atoms.

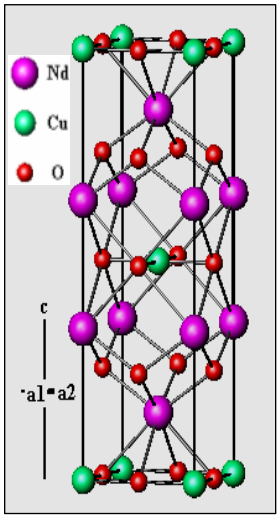

Fig. 12. Unit cell of phase C=Nd_2CuO_4.

In the phase C (Fig. 12) the atom of Nd is eight-coordinated by four oxygen atoms lying on the mixed Cu-O layer in distances 2.676Å and other four on the pour oxygen layer in distances 2.326Å. The Cu atom is tetragonally coordinated by four oxygen atoms in distances 1.972 Å.

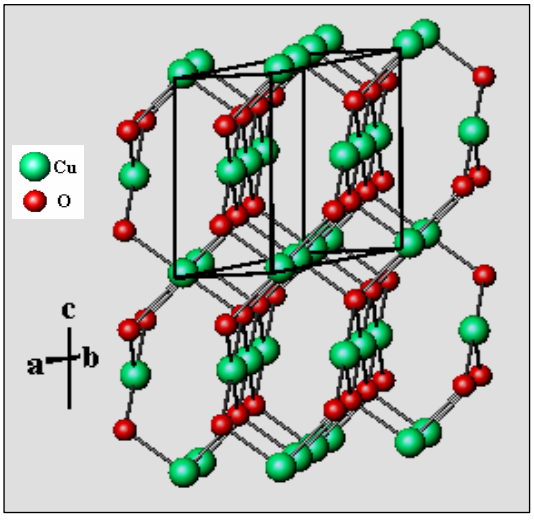

Fig. 13. Crystal structure of phase D=CuO.

The last phase D (Fig. 13) is one of the initial members of synthesis. The copper atom is four coordinated by two atoms in 1.86Å and two other in 2.063Å, forming a distorted rectangle, the center of which is occupied by the Cu atom.

5. Conclusions

Applying the chemical equation

$$(x/2)Nd_2O_3+(1-x)BaCO_3+CuO \rightarrow Nd_xBa_{1-x}CuO_y, \text{ where } x=0.2, 0.4, 0.6, 0.8,$$

we would expect to get a single phase materials of type $Nd_xBa_{1-x}CuO_y$. This expectation was realized fully for x=0.4 and 0.6 and partially for x=0.2 and 0.8. In the second case, in the same time were prepared also the phase B=$BaCuO_2$ for x=0.2, and C=Nd_2CuO_4 and D=CuO for x=0.8.

This means that except the temperature (930°C) significant role plays the atomic proportion Nd/Ba. Thus for proportion 4/6 and 6/4 is encouraged the production of the single phase material, while for proportion 2/8 or 8/2 is encouraged the production of two and three phases. For the last proportion between the products is also the phase CuO. The existence of this phase means that the original quantity of CuO does not fully react, and it is in excess under the above conditions. Based on the found crystal structure of phases A and C we can say that they are superconductors, since as it is resulted from bibliography, the phases $NdBa_2Cu_3O_{6.94}$ and $NdBa_2Cu_3O_{6.78}$, with lightly different oxidation degree, gave more different critical temperatures, T_c~92K and ~63K respectively [15], while the C phase presents a lower T_c near the 23K [14].

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