

# Crystallographic study of mixture $\text{Ba}_{0.6}\text{Nd}_{0.4}\text{CuO}_y$ , in the range of annealing temperatures $860^\circ - 910^\circ\text{C}$

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A powder mixture of  $\text{BaCO}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{CuO}$  was prepared according to the chemical formula  $\text{Ba}_{0.6}\text{Nd}_{0.4}\text{CuO}_y$ . The mixture was heated successively for several hours (52 to 75h) in free atmosphere at temperatures  $860^\circ\text{C}$ ,  $870^\circ\text{C}$ ,  $880^\circ\text{C}$ ,  $890^\circ\text{C}$ ,  $900^\circ\text{C}$  and  $910^\circ\text{C}$ . The products were cooled at room temperature and measured by an X-Ray powder diffractometer with Bragg-Brentano geometry and  $\text{CuK}\alpha$  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, "Powder Profile Analysis". The refinement took place progressively, with constant temperature factors for all atoms. Six phases were found for whole of the samples: A= $\text{Ba}_{1.78}\text{Nd}_{1.22}\text{Cu}_3\text{O}_{6.70}$ , B= $\text{BaCO}_3$ , C= $\text{BaCuO}_2$ , D= $\text{BaCuNd}_2\text{O}_5$ , E= $\text{CuO}$ , F= $\text{Nd}_2\text{CuO}_4$ . All phases, except the A, decrease progressively and disappear in  $910^\circ\text{C}$ . The phase A is the main phase, and is the unique phase in the sample of  $910^\circ\text{C}$ . Its space group is P4/mmm and the mean unit cell constants are  $a=b=3.893\text{ \AA}$ ,  $c=11.690\text{ \AA}$ . The percentage of the main phase varies from 38.78% to 100% (w/w), as the temperature increases from  $860^\circ\text{C}$  to  $910^\circ\text{C}$ .

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## 1. Introduction

The materials under study constitute a part of a series of oxides created from mixtures of oxides (or salts) of component elements (Ba, Rare Earth, Cu) by heating in air, at high temperatures (higher than  $850^\circ\text{C}$ ). The aim of this work is the study of conditions under of which the different crystal phases are created and mainly those that present high  $T_c$  superconductivity. As it is known, materials with crystal structure analogous to the system YBCO-123 [1], present high  $T_c$  superconductivity [2]. Moreover, the structural properties of produced compounds and the variation of the crystal phase percentage in the samples were investigated in this paper.

## 2. Materials

A mixture was prepared by mixing of the oxides  $\text{BaCO}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{CuO}$  in proportions 0.6: 0.2: 1. The proportions and the percentages that were used from each component were taken from the program MOLW [3] and are shown in Table 1.

Table 1. Molecular weights, proportions, percentages and weight (gr) of the initial components that were used for  $\text{Ba}_{0.6}\text{Nd}_{0.4}\text{CuO}_y$ .

| Compound                | Molecular weight | Mult. | %     | Weight (gr) |
|-------------------------|------------------|-------|-------|-------------|
| $\text{BaCO}_3$         | 197.348          | 0.60  | 44.64 | 0.4464      |
| $\text{Nd}_2\text{O}_3$ | 336.477          | 0.20  | 25.37 | 0.2537      |
| $\text{CuO}$            | 79.545           | 1.00  | 29.99 | 0.2999      |

The mixture was heated for several hours at temperatures from  $860^\circ\text{C}$  up to  $910^\circ\text{C}$  with a step of  $10^\circ\text{C}$  and was cooled progressively at room temperature. Thus six samples were examined (1 to 6, correspond to  $860^\circ\text{C}$ ,  $870^\circ\text{C}$ ,  $880^\circ\text{C}$ ,  $890^\circ\text{C}$ ,  $900^\circ\text{C}$  and  $910^\circ\text{C}$ ).

## 3. Characterization

XRD diagrams [4] were taken for each preparation temperature. A two-circle diffractometer with Bragg-Brentano geometry [5] and  $\text{CuK}\alpha$  radiation was used for the study. The scan took place from  $5^\circ$  to  $90^\circ$  ( $2\theta$ ) with a step scan of  $0.05^\circ$  and a scan time of 5 sec. The XRD diagrams were studied with the program PLOTPOW [6]. All phases of the samples were defined with the program EVAWIN [7], which uses the PDF2 database [8]. The XRD diagrams of the samples for all preparation temperatures are given in the Fig. 1.

Starting the investigation of XRD diagrams (Fig. 1) from the sample prepared at  $860^\circ\text{C}$ , the following six crystalline phases were identified: A= $\text{Ba}_{1.78}\text{Nd}_{1.22}\text{Cu}_3\text{O}_{6.70}$  [9], B= $\text{BaCuNd}_2\text{O}_5$  [10], C= $\text{BaCuO}_2$  [11], D= $\text{CuO}$  [12], E= $\text{BaCO}_3$  [13], F= $\text{Nd}_2\text{CuO}_4$  [14]. For the next annealing temperatures, except the A phase, all the remaining phases decrease step by step, as the temperature increases, and disappear in the sample treated at  $910^\circ\text{C}$ . The phase A dominates in all the diagrams and is considered as the main phase. The A phase appears at  $860^\circ\text{C}$  with a low relatively intensity and increases progressively for the next temperatures, in order to remain the unique phase in the

sample annealed at 910 °C. Thus the sample treated at 910 °C is a single phase material.

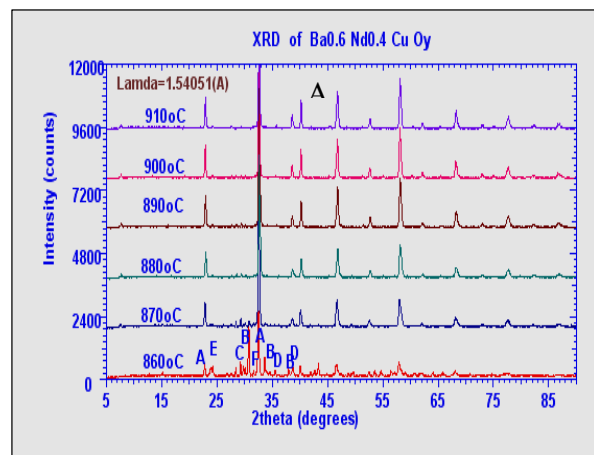


Fig. 1. XRD diagram of the samples prepared in various temperatures.

The peaks characteristics to the first sample (860 °C) present the following image. The stronger peak in all the diagrams is situated at 32.5° and belongs to the A phase. In the first sample (860 °C) the height of this peak is relatively low, but afterwards, it is steadily increased. The peaks shown at 30.7°, 33.6°, 38°, 42.6°, 43.3°, 53.5° and 54.6°, belong to B phase, present a very abrupt decrease for 870 °C and disappear for the next temperatures. The three peaks at 28.4°, 29.4° and 30.1° belong to the C phase. They diminish progressively until they disappear at 910 °C. The peaks at 35.5° and 38.7° belong to phase D and the double peak at 20° belongs to phase E. These two phases (D and E) disappear after 870 °C. The peak at 31.6° belongs to F phase and appears only at 860 °C and 870 °C. Generally, the investigation of all the samples shows a progressive predominance of the main phase A ( $\text{Ba}_{1.78}\text{Nd}_{1.22}\text{Cu}_3\text{O}_{6.70}$ ) and a progressive reduction of secondary phases B, C, D, E, F as long as the samples were heated from 860 °C to 910 °C.

#### 4. Crystal structure refinement

After the characterization of the samples with PDF data-base, the initial crystal structure parameters (space group, unit cell constants and atomic coordinates) of the identified crystalline phases were taken from ICSD data-base and refined, using the Rietveld's method (Powder Profile Analysis). Refinement of the structure parameters of the six phases was achieved with the program DBWSWIN [15], which makes application of the Rietveld method [16]. The refinement took place step-by-step for each phase and for all together finally. In all 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  $R_p$  fluctuate between 0.0636 and 0.0757. The heating duration, the space groups, the unit cell constants and the standard deviations of all phases are given in Table 2. The percentages of phases and the R-factors for each annealing temperature are given in Table 3.

Table 2. Heating duration-temperatures, phase names, space groups and unit cell constants of all phases as they resulted from the Rietveld analysis. A= $\text{Ba}_{1.78}\text{Nd}_{1.22}\text{Cu}_3\text{O}_{6.70}$ , B =  $\text{BaCuNd}_2\text{O}_5$ , C =  $\text{BaCuO}_2$ , D= $\text{CuO}$ , E= $\text{BaCO}_3$ , F= $\text{Nd}_2\text{CuO}_4$ .

| Sample | T (°C) | Time | Phase | Space Group | a b                  | c β                  |
|--------|--------|------|-------|-------------|----------------------|----------------------|
| 1      | 860    | 75h  | A     | P4/mmm      | 3.8995(7)            | 11.664(4)            |
|        |        |      | B     | P4/mbm      | 6.6987(6)            | 5.8166(7)            |
|        |        |      | C     | Im3m        | 18.295(2)            |                      |
|        |        |      | D     | C1 2/c      | 4.757(4)<br>3.355(2) | 5.290(4)<br>99.99(3) |
|        |        |      | E     | Pmcn        | 5.308(3)<br>8.903(5) | 6.439(4)             |
|        |        |      | F     | I4/mmm      | 3.9390(7)            | 12.162(4)            |
| 2      | 870    | 64h  | A     | P4/mmm      | 3.8932(5)            | 11.666(3)            |
|        |        |      | B     | P4/mbm      | 6.697(2)             | 5.815(2)             |
|        |        |      | C     | Im3m        | 18.300(3)            |                      |
|        |        |      | F     | I4/mmm      | 3.941(2)             | 12.165(9)            |
| 3      | 880    | 56h  | A     | P4/mmm      | 3.8933(4)            | 11.690(3)            |
|        |        |      | C     | Im3m        | 18.327(8)            |                      |
| 4      | 890    | 72h  | A     | P4/mmm      | 3.8907(2)            | 11.703(1)            |
|        |        |      | C     | Im3m        | 18.328(6)            |                      |
| 5      | 900    | 52h  | A     | P4/mmm      | 3.8899(2)            | 11.709(1)            |
|        |        |      | C     | Im3m        | 18.327(7)            |                      |
| 6      | 910    | 74h  | A     | P4/mmm      | 3.8900(2)            | 11.707(1)            |

Table 3. Percentages of phases and R factors for all the samples, after the Rietveld analysis.

| Sample | T (°C) | Phase |      |      |      |     |     | $R_p$ % | $R_{wp}$ % | $R_{exp}$ % |
|--------|--------|-------|------|------|------|-----|-----|---------|------------|-------------|
|        |        | A     | B    | C    | D    | E   | F   |         |            |             |
| 1      | 860    | 36.9  | 31.3 | 13.9 | 10.3 | 5.6 | 2.0 | 7.09    | 9.36       | 6.96        |
| 2      | 870    | 88.1  | 3.7  | 7.5  | -    | -   | 0.7 | 7.57    | 9.65       | 6.94        |
| 3      | 880    | 96.9  | -    | 3.1  | -    | -   | -   | 7.72    | 9.69       | 7.30        |
| 4      | 890    | 97.0  | -    | 3.0  | -    | -   | -   | 6.36    | 8.22       | 6.60        |
| 5      | 900    | 97.9  | -    | 2.1  | -    | -   | -   | 6.90    | 9.02       | 6.91        |
| 6      | 910    | 100   | -    | -    | -    | -   | -   | 7.09    | 9.36       | 6.96        |

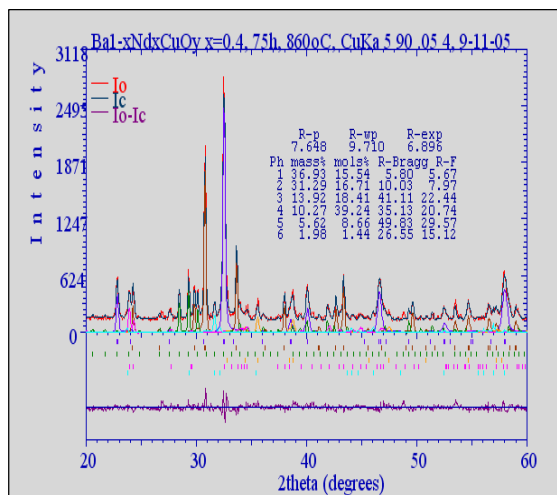


Fig. 2. Results of Rietveld analysis for the sample of 860 °C.

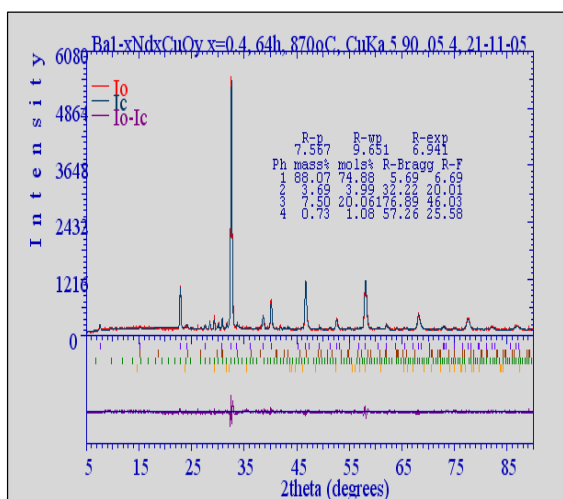


Fig. 3. Results of Rietveld analysis for the sample of 870 °C.

The results of refinement with the Rietveld analysis for three of the six samples (860 °C, 870 °C, 910 °C) are presented in the Figs. 2, 3 and 4. The non presented samples (880 °C, 890 °C, 900 °C) present inappreciable changes and for this reason were omitted. In these figures, the diagrams of intensities  $I_o$  and  $I_c$  (observed and calculated) as an interrelation of  $2\theta$  are shown. The degree of agreement between  $I_o$  and  $I_c$  is given in the down part of the figures with a diagram that it shows the difference  $I_o-I_c$ .

The positions of reflections of various phases are presented in the down part of figures with thin 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 Fig. 2, while the Miller indices of reflections are shown on the upper place of the Fig. 4, only for the single phase sample treated at 910 °C.

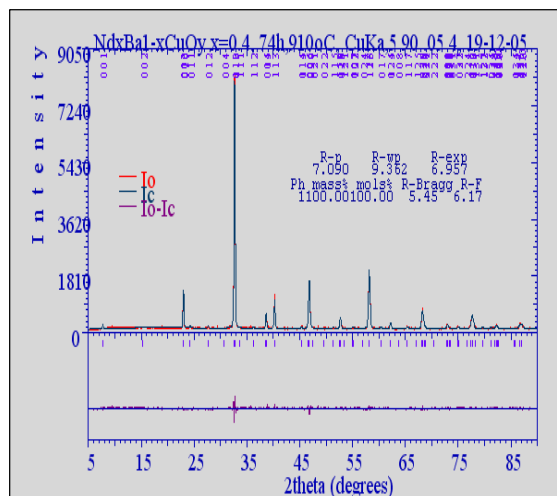


Fig. 4. Results of Rietveld analysis for the sample of 910 °C.

## 5. Analysis of the structures and discussion

The analyses of the six samples and their refinement resulted in six phases (A,B,C,D,E,F). All these phases exist in the sample 1. As it is shown in Table 3, the first phase (A) is the main phase, exhibiting an increase of its percentage from 36.9 % to 100 %, in the series 1 to 6. Its maximum percentage corresponds to temperature of 910 °C. For this annealing temperature a unique phase is present. The phases B and F exist only in the samples 1 and 2, while the phase C exists in the samples 1 to 5 with decreasing percentage. The phases B and F present an abrupt fall of percentage in the sample 2 and disappear in the next samples. This fact means that the A phase is amplified for higher temperatures, as opposite to phases B and F that are stimulated for lower annealing temperatures. The initial components CuO and  $\text{BaCO}_3$  (phases D and E) exist only in the first sample, which means that these did not react completely with the other components at the temperature of 860 °C. Neodymium is distributed in the three phases A, which exists in all the samples, and the B and F phases which exist only in the samples 1 and 2 (860 °C and 870 °C). In the next paragraphs the structures of the three phases will be examined briefly.

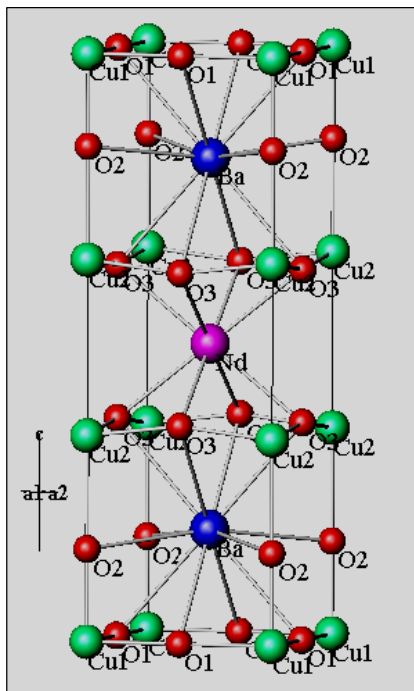


Fig. 5. Unit cell of main phase A ( $\text{Ba}_{1.78}\text{Nd}_{1.22}\text{Cu}_3\text{O}_{6.7}$ ).

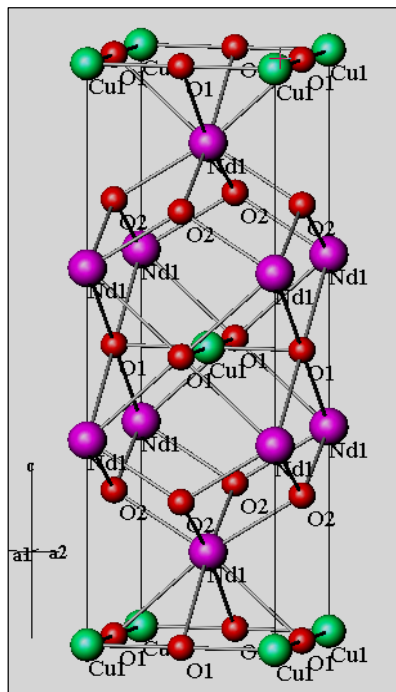


Fig. 6. Unit cell of phase F ( $\text{Nd}_2\text{CuO}_4$ ).

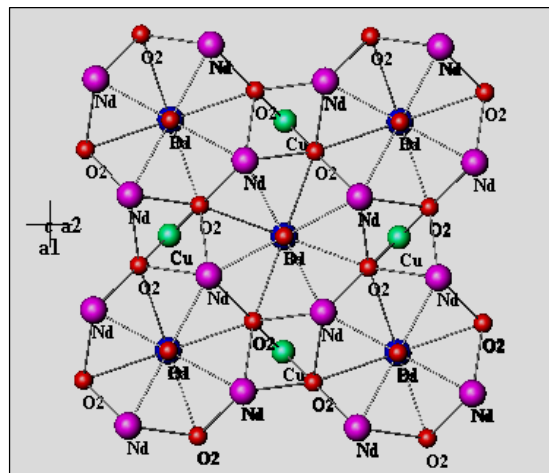


Fig. 7. The structure of phase B ( $\text{BaNd}_2\text{CuO}_4$ ), viewed parallel to  $c$  axis.

The structure of the main phase is shown in Fig. 5. In this there are three layers of Cu-O, the first one of which at  $z=0$  and the two others at about  $z=0.35$  and  $z=0.65$ . The last two layers have a thickness about  $dz=0.02$  (or  $\sim 0.23\text{\AA}$ ), since the Cu atoms are at  $z=0.35$  and  $0.65$  and the oxygen atoms are at  $z=0.37$  and  $0.63$ . The Ba atoms are coordinated by twelve oxygen atoms found at three layers. The four of these are at the first Cu-O layer ( $z=0$ ) and the four others at the second Cu-O layer ( $z=0.37$ ). The remaining four oxygen atoms are in the same plane with the Ba atoms. The Nd atoms, at the middle of the unit cell, are coordinated with eight oxygen atoms which lie on the two thickness Cu-O layers (four at  $z=0.37$  and four at  $z=0.67$ ). This is a characteristic superconducting structure, with a high  $T_c$  about the 96 K [9].

The structure of the F phase is shown in the Fig. 6. In this the Nd atoms are coordinated with eight O atoms and the Cu atoms are coordinated with four O atoms on the apices of squares, the centres of which are occupied by the Cu atoms. There are two such parallel planes in each unit cell, but from the structure miss the single parallel Cu-O layers, essential for the existing of the superconducting properties. The oxygen atoms lie on two types of planes. The first of these is formed with Cu and O atoms and the second one only with O atoms. The O atoms of two planes are connected via the Nd atoms which lie on an intermediate plane. This part of structure is repeated along the  $c$  axis. In the B phase (Fig. 7) the Ba atoms are coordinated by eight oxygen atoms, while the Nd atoms with six O atoms. Each of the Cu atoms is coordinated with four O atoms on the apices of a square, the centre of which is occupied by the Cu atom. The planes of the successive squares are perpendicular each to other. From this structure miss the single parallel Cu-O layers, essential for the existing of the superconducting properties.

The remaining phase structures (C, D and E), as defined after refinement, are in accordance with those reported in bibliography, with some slight variations.

In order to find the precise chemical type of the phase A we proceeded as follows. From the refinement of the

population parameters of Ba sites (2h) was found lightly larger than unity ( $pp=1.008$ ). That means the sites are occupied mainly by Ba atoms and partially by the heavier Nd atoms. Thus, after the analysis of the populations for this site, the  $pp$  corresponding to Ba is 0.89 and to Nd 0.11. Also, the populations of  $\text{O}_1$  and  $\text{O}_2$  sites (2f and 4i) are lower than unity. The sites of Nd (1d), of  $\text{Cu}_1$  (1a), of  $\text{Cu}_2$  (2g) and  $\text{O}_2$  (2g) are fully occupied by the same kind of atoms. With this analysis the final chemical formula of the phase A is  $\text{Ba}_{1.78}\text{Nd}_{1.22}\text{Cu}_3\text{O}_{6.70}$ . This formula is in good agreement with the initial synthesis composition of the sample  $[(\text{Ba}_{0.6}\text{Nd}_{0.4}\text{CuO}_y)_{x3}=\text{Ba}_{1.8}\text{Nd}_{1.2}\text{CuO}_{3y}]$ .

## 6. Conclusions

In this paper the chemical and the structural behavior of Cu and Ba in the presence of Nd was evidenced. As it was found, in order to react the total quantities of the initial components  $\text{CuO}$  and  $\text{BaCO}_3$  the temperature must be higher than 860 °C. From the three phases which contain Nd, the phases B and F are stimulated for lower annealing temperatures, while the main phase A is stimulated in higher temperatures. The A phase appears with a concentration of 36.9 % for lowest temperature of annealing and goes up to 100 % for 910 °C, where becomes a unique phase. The structure of the phase A explains the existence of superconductivity in the studied samples.

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