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Isovalent Substitutions and the Number of Oxygen Atoms by Chains Control of Structure and Superconductivity in High T_c Superconductors

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***Abstract*—We report here on the preparation, X-ray diffraction with Rietveld refinement and the effect of heat treatments in $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$**($x$ = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1). **Each sample was subject to two types of heat treatment: oxygen annealing [O] and argon annealing followed by oxygen annealing [AO]. When x increase from 0 to 1, the ratio a/b increases and T_c decreases. For each *x*, the [AO] heat treatment decreases the ratio a/b (for $0 \leq x < 1$), the distance d[Cu(1) - (Sr/Ba)] for x < 0.25 and T_c(for *x* < 0.2).** However, **the [AO] heat treatment increases the T_c (for x > 0.2)** with **the ratio a/b by 9.16 K to 77.2 K for x=1. Note that the crystalline parameter b is constant but a (and c) increases indicating an increase of the number of oxygen atoms by chain (NOC) along a axis leading to a increases of a/b (T_c) toward a tetragonal structure. For x = 0.2, the basal surface of the sample a.b = s[O] ≈ s[AO] with $T_c[O] \approx T_c[AO]$=80 K. Remarkable correlations were observed between $T_c(x)$, the volume of the unit cell V(x) and $d[Cu_{(1)}$-(Sr/Ba)](x). A combination of several factors such as the decrease in d[Cu(1)-Sr/Ba]; the increase in cationic and the NOC order and in-phase purity for the [AO] samples may account the observed data.**

***Keywords*—High-Tc superconductors, X- ray diffraction. AC magnetic susceptibility, NOC, Tc, surface ab, distanced[Cu(1)-Sr/Ba], Heat treatments**

I. INTRODUCTION

The effect of substitution on the structural and superconducting properties of $YBa_2Cu_3O_{6+z}$ has beenextensively investigated [1]. There are at least four distinct crystallographic sites which (excluding that of oxygen) Y, Ba, Cu plane, and Cu chain can be substituted with different elements.

Single-phase $LnBa_2Cu_3O_{6.95}$ (Ln = rare earth) in bulk form can be prepared with the critical temperature T_c close to 92 K. All these compounds show anorthorhombically distorted oxygen-deficient tripled-perovskite structure and both the orthorhombic distortion and T_c depend sensitively on the oxygen content (6+z) [2]. It is interesting to check if an isovalent substitution of Ba^{+2} by Sr^{+2} with smaller radius, would modify some of the results discussed above when Y^{+3} is replaced by the rare earth Nd^{+3} with bigger ionic radius. We have studied the structural and superconducting properties of the superconductor $NdBaSrCu_3O_{6+z}$ [3]. This compound when annealed in oxygen at 450°C showed a tetragonal structure and a T_c of 79 K. When the same sample was heated in argon followed by oxygen annealing; we observed an orthorhombic structure and an increase of T_c by 6 K. So T_c depends also on heat treatment.

With these in mind we have investigated the effect of isovalent substitutions and the number of oxygen atoms by chains on the structural and superconducting properties of $(Y_{1-x}Nd_x)(SrBa)Cu3O_{6+z}$(0, 0.2, 0.4, 0.5, 0.6, 0.8, 1) compound. We found that the influence of argon heat treatment on these properties depended on Nd content, x.

II. EXPERIMENTAL TECHNIQUES

The polycrystalline samples have been prepared by solid-state sintering of the respective oxides and carbonates. The chemicals were of 99.999% purity except in the case of $BaCO_3$ which was 99.99% pure. Nd_2O_3, $SrCO_3$, $BaCO_3$ and CuO were thoroughly mixed in required proportions and calcined at 950°C in air for a period of 12-18h. The resulting product was ground, pelletized and heated in air at 980°C for a period 16-24h. This was repeated twice. The pellets were annealing in oxygen at 450°C for a period of 60-72h and furnace cooled. This was denoted as sample [O] for each x. XRD data of the sample ware collected with Philips diffractometer fitted with a secondary beam graphite monochromator and using CuK_α (40 kV/20 mA) radiation. The angle 2θ was varied from 20° to 120° in steps of 0.025° and the courting time per step was 10 sec. The XRD specters were refined with Rietveld refinement [4].

Superconducting transitions were checked by measuring both the real χ' and the imaginary χ'' parts of the AC susceptibility as a function of temperature in a field of 0.11 Oe and at a frequency of 1500 Hz.

For each x, the same sample [O] was then heated in argon at 850°C for about 12h, cooled to 20°C and oxygen was allowed to flow instead of argon and the sample was annealed at 450°C for about 72h. This sample is denoted as [AO]. XRD and AC susceptibility measurements were performed on a part of this sample.

III. RESULTS AND DISCUSSION

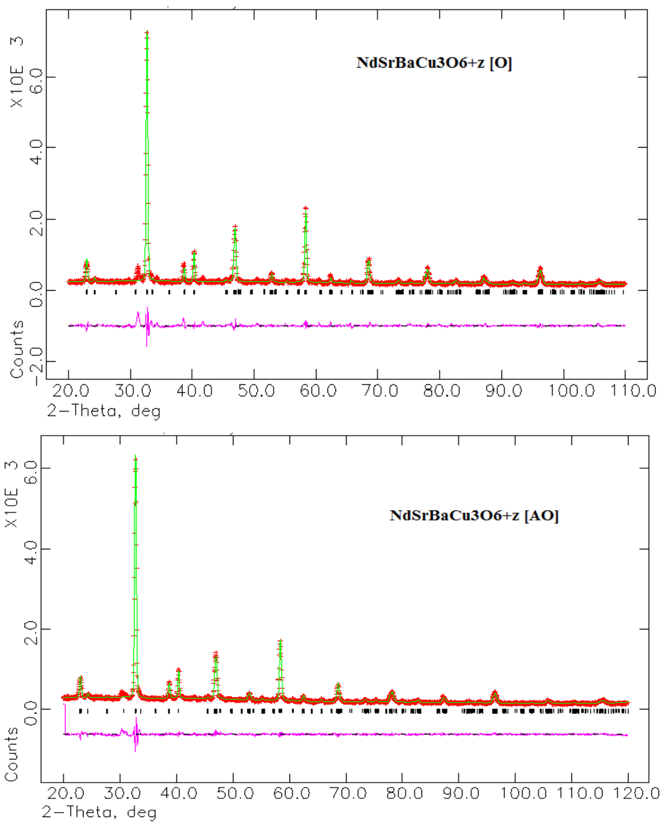

Fig.1: XRD pattern of $NdSrBaCu_3O_{6+z}$, observed, calculated with Rietveld refinement and difference profiles for sample [O] and sample [AO].

As example, the measured XRD patterns and calculated with Rietveld refinement in the case of $NdSrBaCu_3O_{6+z}$ ([O] and [AO]) are shown in figure 1. In general, the samples were well crystallized and the reflections were sharper after the [AO] heat treatment. The orthorhombic splitting was also influenced by the [AO] treatment. Some weakunidentified impurity peaks α (at 2θ=31°) were seen in the [O] samples. They disappeared after the [AO] heat treatment. This indicates an improvement of crystallographic quality of the samples [AO].

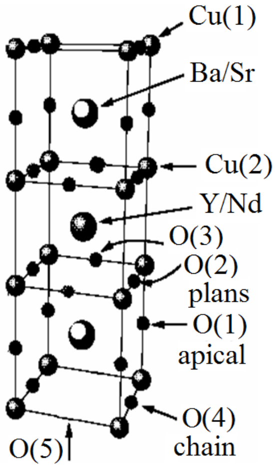

Fig. 2: The unit cell of the compound $Y_{1-x}Nd_xSrBaCu_3O_{6+z}$.

In order to determine the coordinates of these atoms (i.e. the positions of the atoms in the unit cell), we chosen the reference (a,b,c) with origin at Y/Nd site. The atoms of the basal plan have the following fixed coordinated: Cu(1) (0.5,0.5,0.5), O(4) (0,0.5,0.5) and O(5)(0.5,0,0.5), while those of the other atoms O(1), O(2), O(3), Cu(2) and Sr/Ba vary along the z axis. The positions of the atoms in $Y_{1-x}Nd_xSrBaCu_3O_{6+z}$ are schematized in Figure 2.

Figure 3 illustrates the evolution of the lattice parameters a, b, c and the surface s as function of the x(Nd) and the heat treatment. Figure 3. (a) shows that the two curves c[O] and c[AO] are identical. It indicates that the parameter c does not depend on the heat treatment but depends only on the composition x(Nd). The parameter c increases with x in agreement with the fact that $r(Nd^{3+})$ = 0.995 Å is superior to that $r(Y^{3+})$= 0.893 Å.

The effect of the heat treatment on the basal surface s(x)

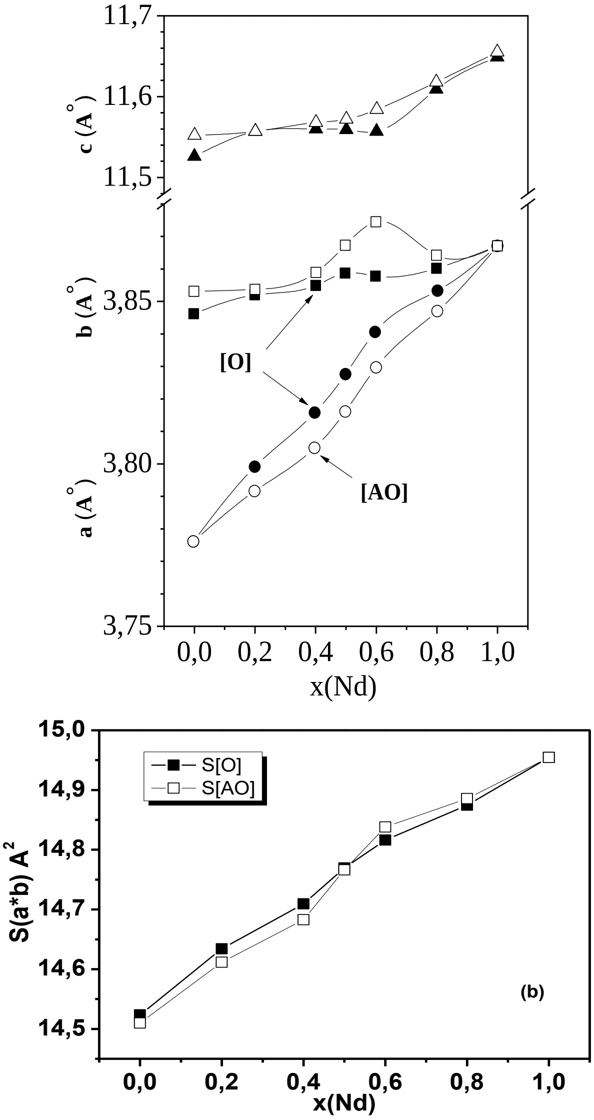

Fig.3: Variation of the parameters a, b and c (a) and surface s (b) of $Y_{1-x}Nd_xSrBaCu_3O_{6+z}$ as function of x and the heat treatment.

=ab of the unit cell is remarkable. The Figure 3(b) shows that s[AO] < s[O] for $x \leq 0,5$ (with $T_c[AO] < T_c[O]$ for $x \leq 0,2$).

This effect is reversed for $x > 0.5$. We notice that for x=1, s[AO] =s[O] with $T_c[AO]$ =77,18 K and T_c [O] = 68,023 K. These results show that T_C depends on the surface s, i.e. of order/disorder of oxygen in the basal plane. We have also obtained the same curve of T_c as function of s and the volum as a function of s and the heat treatment in Figure 5. This shows again that the heat treatment does not influence the parameter c.

Figure 4(a) shows the a/b ratio as function of x (Nd) and the heat treatment. The increase of a/b[O] from 0.982 ($a\neq b$) for x = 0 to 0.998 ≈1 (with a=b) for x = 1. While for the samples [AO], a/b[AO] increases from 0.980 for x=0 (for $YBaSrCu_3O_{6+z}$) to 0.998 for x=1 ($NdBaSrCu_3O_{6+z}$). These results indicate a structural phase transition from orthorhombic to tetragonal.

For each x, the heat treatment [AO] decreases the a/b ratio. Thus, the heat treatment influences the parameters a and b, but not c, i.e. the order/disorder of oxygen in the basal plan ab, and consequently impacts the number of the holes in the $Cu(2)O_2$ copper planes. As seen in Figure 4(b), when x increase from 0 to 1, the ratio a/b increases; and $T_c[O]$ decreases whereas the $T_c[AO]$ decreases at x=0.2, increases until x=0.6 and after it decreases to 77,18 K for x=1.

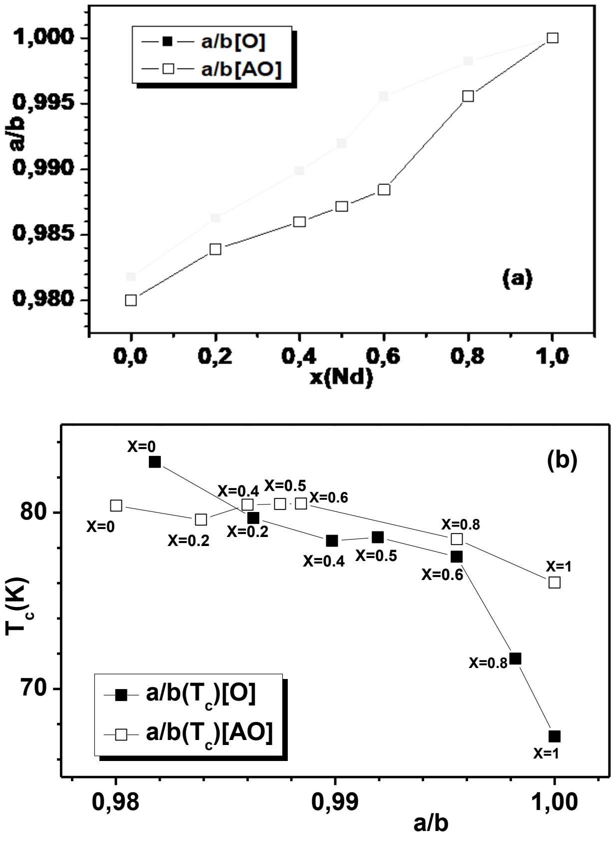

Fig.4: (a): The a/b ratio of $Y_{1-x}Nd_xSrBaCu_3O_{6+z}$ as function of x and the heat treatment. (b): Variation of the ratio a/b as a function of Tc and heat treatments of $Y_{1-x}Nd_xSrBaCu_3O_{6+z}$.

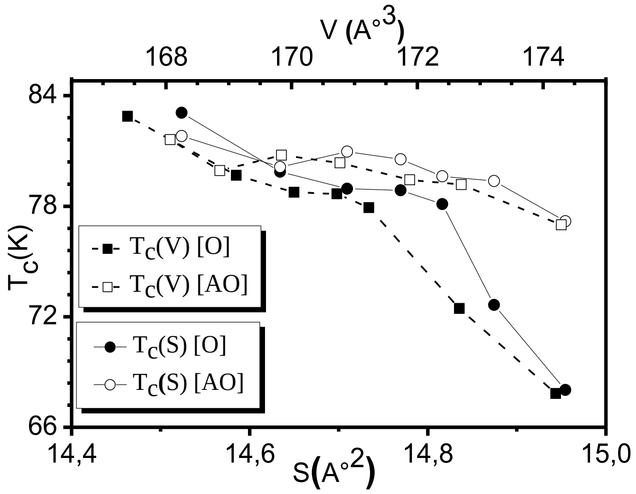

Fig.5: The critical temperature as function of the volume, the surface of the unit cell and the heat treatment in $(Y_{1-x}Nd_x)BaSrCu_3O_{6+z}$.

The high critical temperature T_c of superconductors' oxides strongly depends on the concentration of the holes on the two-dimensional layers $Cu(2)O_2$. The universal relation between standardized $T_c(\tau_c=T_c/T_{cmax})$ and the concentration p_{sh} of the holes in the $Cu(2)O_2$ plane of superconductors oxides (La214 , Y123, Bi2212, Bi2223, Tl2201 and Tl1212) shows that T_c independent of the considered sample [5].

The existence of the plateau for $0.12 < p_{sh} < 0.25$, in which the critical temperature is maximal (τ=1) [5], is observed experimentally. Particularly in the universal correlation between T_c and n_s/m^*(the ratio of the density of the holes and the effective mass) given by Uemura et al [6]. An increase in T_c, of a system to another, is related to a decrease of m^* and an increase of n_S.

A correlation between the critical temperature and the oxygen arrangement in the layers of the compound $(Cu,C)Ba_2Ca_2Cu_3O_{9-\delta}$ was given by N. Iliev et al. [7]. It is based on the fact that the variation of the rate of oxygen in these layers influences the content of the holes (p_{sh}) in the plans of conduction $Cu(2)O_2$. Thus, M. R. Presland et al [8] obtained a parabolic relation between T_c standardized $\tau_c = T_c/Tc_{max}$ and the concentration of the holes p_{sh}.

Typically, when doping rises from p=0.06, the critical temperature T_c increases from zero to attain its maximal value T_{cmax} at p=0.16. This is accompanied by the reduction of the pseudo gap energy E_g du to the depression in electron density of states. At critical doping level p=0.25, the pseudo gap phase eventually vanishes and further increase of doping is characterized by decrease of T_c and disappearance of superconductivity at p≈0.30.

The following empirical relationship between T_c and p has been found in experiments to hold for a wide class of high T_c cuprates. The determination of p_{sh}, is estimated by equation (1) from the T_c measured in a sample, where Tc_{max} is 93K in the case of cuprates [9].

$$T_c(p_{sh})=T_{cmax}[1-82.6(p_{sh}-0.16)^2] \qquad (1)$$

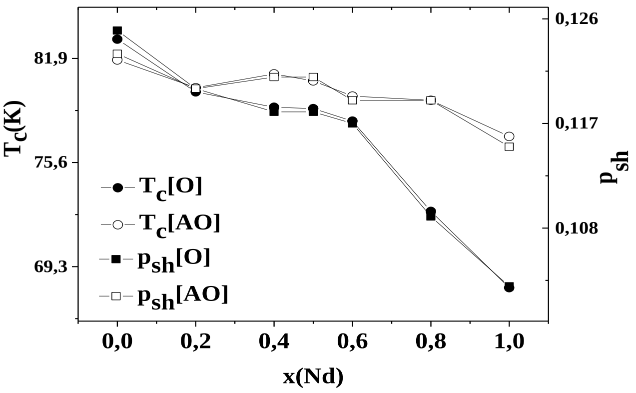

Fig.6 **:** Correlation between the number of the holes p_{sh} the critical temperature as function of x(Nd) and the heat treatment in $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$.

We have obtained a correlation between the number of the holes p_{sh} and the critical temperature T_c as function of x(Nd) and the heat treatment in $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$ in (figure 6).

The correlation between T_c with ρ_{Sh} as a function of distance d[Cu(1)-(Sr/Ba)] between the copper Cu(1) of the chains and the site of Sr/Ba and the heat treatment is shown in the Figure 7. We obtained a remarkable correlation between this distance (d[Cu(1)-(Sr/Ba)]) with T_c as a function of x and the heat treatment as seen in Figure 8. In the unit cell (Figure.2), the copper Cu(1) is fixed; therefore, the variation of the distance d[Cu(1)-(Sr/Ba)] is the result of the displacement of the site Sr/Ba along z.

For a given heat treatment, when the critical temperature T_c(x) increases the distance d[Cu(1)-(Sr/Ba)](x) decreases in Figure 7 and 8. The attraction force via the intermediate apical oxygen O(1) makes it possible to increase T_c. This apical oxygen plays the role the bridges linking charge reservoir and CuO_2 conducting layers for highs superconductors (HTS) [10].

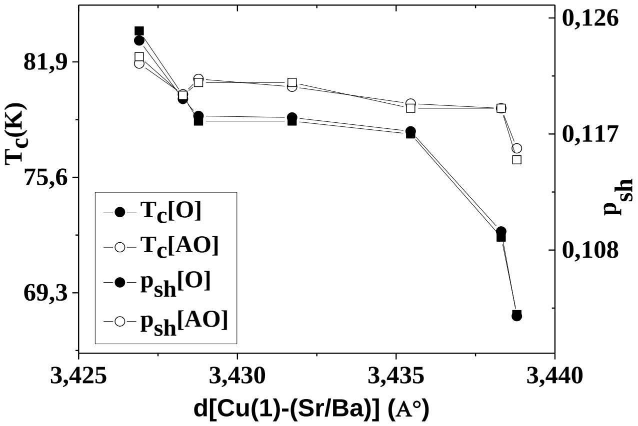

Fig. 7: The critical temperature and the number of holes p_{Sh} as function of x(Nd) and heat treatment in $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$.

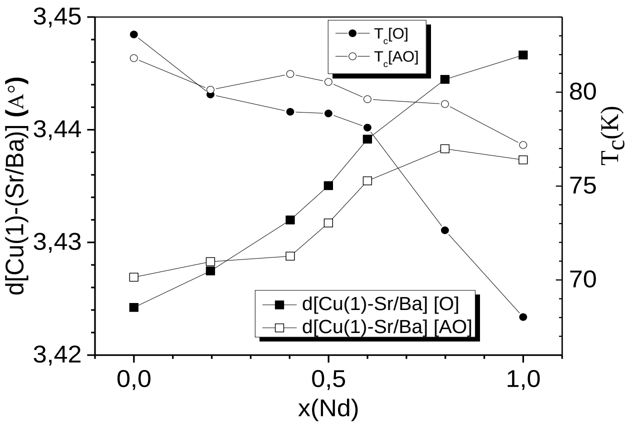

Fig.8**:** The distance d[$Cu_{(1)}$-(Sr/Ba)] and the critical temperature as function of x(Nd) and heat treatment in $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$.

The reduction of the number of holes in the CuO_2 planes makes it possible to increase the parameter c in $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$ [O] (Figure. 9). It is the same behavior of the figure obtained by Ruixing Liang et al [11] in the case the doping p of $YBa_2Cu_3O_{6+z}$ as a function of the lattice parameter c. The c-direction unit cell length is the sum of bond lengths, c = 2d[Cu(1)-O(1)]+d[Cu(2)-Cu(1)]+2d[Cu(2)-O(1)]. The change in c is mainly caused by the change in d[Cu(2)-O(1)] because it is much more sensitive to change in the oxygen content than other bond lengths [11]. This result can also be justified by the Figures (6 and 8)[O], such that the parameter c[O] increases with the distance d[Cu(2)-Cu(1)][O]. Indeed the critical temperature T_c[O] and p_{sh}[O] increase when x decreases, but the distance d[Cu(2)-Cu(1)][O] decreases which also reduces the parameter c[O]. The parameter c increases when the oxygen content decreases in the basal plane of the samples $REBa_2Cu_3O_y$ (RE=Gd, Er) [12].

The latter decreases with the doping p [11]. The maximum critical temperature is obtained in the tetragonal structure with the crystal parameter a=0.385nm. In the compounds $REBa_2Cu_3O_7$ (RE=rare-earth elements) T_c=92K [13] and in the compound $NdBaSrCu_3O_{6+z}$[O], T_c=68,02K in the $Cu(2)O_2$ plane on the superconducting property by the influence on the parameter a (a = $2d_{Cu(2)-O(2)}$ = $2d_{Cu(2)-O(3)}$), compared with that obtained by Wang et al. [14] (T_c = 80 K). This also shows that the role played by the number of holes.

The critical temperature T_c varies as a function of the n number of $Cu(2)O_2$ planes in $Ba_2Ca_{n-1}(CuO_2)n(O,F)_2$ [15]**.** It is maximal for n = 3 and constant from n = 5. It is evident that the crystal parameter c increases with the number n of the $Cu(2)O_2$ planes. This increase is linear in the case of $Sr_2Ca_{n-1}Cu_nOy$ (n = 3-7) [16]. Piyamas Chainok et al [17] synthesized the $YBa_mCu_{1+m}O_{(2m+3)-x}$ superconductors; m = 2, 3, 4, 5 that were Y123, Y134, Y145 and Y156 by solid state reaction. They found that the T_c^{onset} of Y123, Y134, Y145 and Y156 were at 97, 93, 91 and 85 K. The Y123 has two CuO_2 planes and one CuO chain. In 2009, Aliabadi et al [18] synthesized Y358 ($Y_3Ba_5Cu_8O_{18}$) superconductor by solid state reaction that becomes superconducting above 100 K with the lattice parameters a = 3.888 Å, b = 3.823 Å, c = 31.013 Å. The Y358 has crystal structure similar to Y123 with five CuO_2 planes and three CuO chains. So, the increase in the number n of $Cu(2)O_2$ planes and Cu(1)O chain have important effect on the T_c of YBaCuO superconductors.

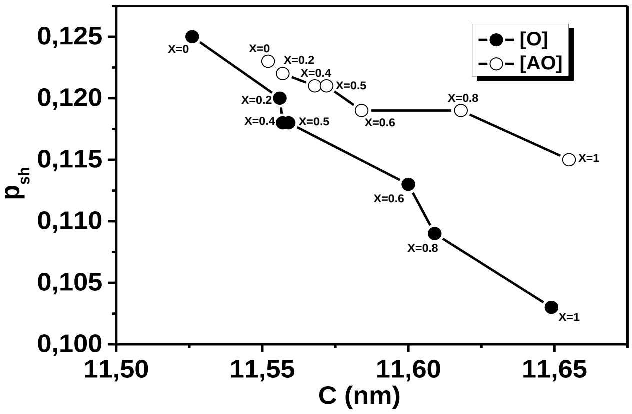

Fig. 9: The number of holes p_{Sh} of $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$ as a function of the lattice Parameter c.

Isovalent substitution doping (here substitution of Y^{+3} by Nd^{+3}) changes the number of holes in the $Cu(2)O_2$ plans, the chemical substitution unavoidably introduces disorder into the crystalline lattice due to random distribution of dopant atoms. The effect of the doping disorder on T_c has become a recent concern. This effect of holes p on T_c has been systematically studied for the cuprates based copper oxide superconductors by several authors [2, 19].

This is identical to the model of transfer of the charge from the chains towards the $Cu(2)O_2$ plans. Thus, T_c increases while d[Cu(1)-(Sr/Ba)] decreases.

When x increases from 0 to 1, the cation and anion disorder increases (reduction of number oxygen by Chain NOC [20]) in the samples [O]. Thus, the concentration p_{sh} of holes (or T_c) of these samples [O] decreases (Figures 5 and 6). The treatment [AO] reduces the atomic disorders (increase inthe NOC), which increases p_{sh} (or T_c) [9, 20]. For a given x, the heat treatment [AO] increases p_{sh} and T_c for x ≥ 0.2. It should be noted here that, while x increases, the concentration p_{sh} of holes (or T_c) of samples [AO] decrease; in the first time, from x=0 to x=0.2 and increases after.

We note that the parameter a increases with x and parameter b remains almost constant. The increase in parameter a is attenuates in the samples [AO]. The surface s increases linearly. When x increases from 0 to 1, a/b[O] increase from 0.982 to 1 indicating a transition of structural phase from orthorhombic to tetragonal. The increase in a/b[AO] (from 0.980 for x=0 to 0.995 for x=1) is attenuated indicating also a transition of structural phase from orthorhombic to tetragonal. For a given x, the heat treatment [AO] decreases a/b. The later increases with x. This is a sign of the reduction in the cation and anion disorders with x. When x increases from 0 to 1, T_c[O] decreases but a/b [O] increases. Then for x > 0.2, T_c [AO] and a/b[AO] increases as expected in RE123 [13]. Recently, Ana Haraborand al. [21] use our argon-oxygen heat treatment to improve the superconducting properties in the YBCO-123samples.

IV. CONCLUSIONS

Our study is based on the research of the parameters which influence the structural and superconductive property in $(Y_{1-x}Nd_x)SrBaCu_3O_{6+z}$. By using two heat treatments ([O] and [AO]), we have obtained different critical temperatures in the same compound (T_c[O] ≠T_c[AO]). For each x, the a/b[O] ratio is higher than a/b[AO] ratio. Thus, the critical temperature T_c increases and a/b ratio decreases, except in the case of x≥0,2 for sample [AO], where a/b ratio increases with T_c.

The heat treatment influences the parameters a and b, the surface s, the a/b ratio and the critical temperature T_c. The variation of the parameters a, b, s and a/b influences the oxygen disorder in the basal plans (or NOC). The transfer of charge between the two coppers, Cu(2) of plane and Cu(1) of chain is effected by the insertion of oxygen in the basal plane or order/disorder oxygen on this plane,via the apical oxygen O(1). This is justified by the correlation between, the number of the holes p_{sh}, the critical temperature T_c and the distance d[Cu(1)-(Sr/Ba)] as function of x(Nd) and heat treatments in $Y_{1-x}Nd_xBaSrCu_3O_{6+z}$..

Several factors like the change of the ionic ionic size of the rare earth Nd in $YBaSrCu_3O_{6+z}$, its disorder on the site (Sr/Ba), the oxygen order of the chains or the surface, atomic distances, heat treatment and the a/b ratio, influence the critical temperature T_c by intermediary of the NOC.

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