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Effects of Isovalents Substitutions and Argon Heat Treatment on the Structural and Superconducting Properties of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$

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***Abstract*— We report here our investigations on the preparation, X-ray powder diffraction with Rietveld refinement, AC magnetic susceptibility measurements, effect of heat treatments and substitution of Y by the rare earth Ln = Eu, Sm and Nd in $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$. Each sample prepared by solid-state sintering at a high temperature under reducing atmosphere, was subject to two type of heat treatment: oxygen annealing [O] and argon annealing followed by oxygen annealing [AO]. In each sample, the [AO] heat treatment increase the orthorhombicity ε = (b – a)/(b + a) (where a and b are the parameters of the unit cell in the basal plane) and the critical temperature T_c. An enhancement of the irreversibility line $H(t=T_p/T_c)$ due to the argon heat treatment was observed. Different correlations were observed between structural, electrical and magnetic properties. Several factors, such as the ionic size r of the rare earth Ln, an increase in cationic and chain oxygen ordering; the number $p_{sh}(r)$ of holes by $Cu(2)O_2$ superconducting planes and in-phase purity of the [AO] samples may account for the observed data.**

Keywords—High-T_c superconductors, Heat treatments, T_c, X-ray diffraction, Orthorhombicity, AC magnetic susceptibility.

I. INTRODUCTION

Most of the extensive research efforts in solid state physics have been directed towards the study of high T_c superconducting cuprates since 1986. It is well known that the physical properties of these compounds are closely related to the conditions of their preparation. The high T_c superconductivity is carried by positive charges (holes) on the highly correlated CuO_2 superconducting planes. The electronic states of the later are sensitive and influenced by structural, electrical and magnetic characteristics, such as the size of the ionic radius, the applied magnetic field, the valence, the distribution of surrounding ions and the oxygen content. Furthermore, all these characteristics are strongly influenced by heat treatments applied during the preparation of the samples. In particular, when Ln is a rare earth element, such as Eu, Sm and Nd, various effects are expected because of large ionic radius of the Ln ions to Y.

Among the most studied compounds are $LnBa_2Cu_3O_{6+z}$ (Ln = Y or Lanthanides) that is stipulated by several reasons: On the one hand, the electric transport characteristics can rather easily be varied by doping of the compound with substituting elements [1,2] or varying the oxygen content. For example when $0 < z < 0.5$, the compound $YBa_2Cu_3O_{6+z}$ is tetragonal and antiferromagnetic insulator and for $0.5 < z < 1$, the compound is orthorhombic, p-type metal and becomes superconducting at low temperatures [3,4,5,6]. For each oxygen content 6+z, T_c increased with the size r of the Ln ions [7,8]. On the other hand, these compounds have a rather high critical temperature $T_c \approx 90$ K above the nitrogen liquefaction temperature [9,10,11].

Many studies have been done on Sr substitution in the compound $Ln(Ba_{1-x}Sr_x)_2Cu_3O_{6+z}$ [12-15]. These authors conclude that: for each Ln, the critical temperature and the orthorhombicity decreases with increasing the concentration x of Sr [12,13,16]. For each x, the crystalline structure and T_c depend on the ionic size r of the Ln ions [17,18,19].

In this paper, the samples have been synthesized at high temperature under effect of two heat treatments ([O] and [AO]). In order to obtain higher solubility of Ln in $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ (where Ln = Eu, Sm and Nd). The powder XRD and AC magnetic susceptibility measurements have been carried out. It is interesting to check if an isovalent substitution of Ba^{2+} by Sr^{2+} with smaller ionic radius would modify some of the results discussed above when Y^{3+} is replaced by Ln^{3+} with bigger ionic radius.

In order to study the role played by the Yttrium and Barium atomic plans and find out the factors conditions which govern the superconductivity in these compounds, we have investigated the structural and superconducting properties of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$. Indeed, the correlations between these properties, with the influence of argon heat treatment and the ionic size of Ln will be discussed.

II. EXPERIMENTAL TECHNIQUES

The polycrystalline samples $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd were synthesized by solid-state reaction 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. Y_2O_3, Ln_2O_3, $SrCO_3$, $BaCO_3$ and CuO were weighted in composition ratio and well mixed and calcined at 950 °C in air for a period of 12 – 18 h. The resulting product was ground, mixed, pelletized and heated in air at 980 °C for a period of 16 -24 h. This was repeated twice. The pellets were annealed in oxygen at 450 °C for a period of 60 -72 h and furnace cooled. This was denoted as sample [O] for each Ln.

Powder XRD data were collected at room temperature by using a diffractometer fitted with a secondary beam graphite monochromator with a CuKα (40 kV/20mA) radiation source. The angle 2θ was varied from 20° to 120° in steps of 0.025° and the counting time per step was 10 sec. The crystalline structure has been refined by Rietveld analysis of powder XRD data. For each sample, the oxygen content value was close to 6.94 ± 0.04, it was determined by the iodometric method.

The sample's magnetic response is sensed by a pick-up coil surrounding the sample. The AC magnetic susceptibility measurements ($\chi_{ac} = \chi' + i\chi''$) as function of temperature in a field of 0.11 Oe were carried out at 1500 Hz. In addition, χ' and χ'' were measured in a static field ($0 < H = H_{dc} < 150$ Oe) superimposed on the AC field of $H_{ac} = 0.11$ Oe.

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

III. RESULTS

A. *Crystalline Structure and real part of the AC magnetic susceptibility*

Fig. 1(a) and (b) shows the powder XRD patterns of the Eu- Sm- and Nd- systems, respectively. The samples were well crystallized and the reflections were sharper and well resolved after the [AO] heat treatment. The lattice parameters determined from the XRD patterns by Rietveld refinement are collected in "table. I". These diffraction patterns confirmed that all samples have the orthorhombic perovskite structure, and no impurity phase was observed after [AO] heat treatment (indicated by cross in fig. 1 (a) disappeared after the [AO] heat treatment). This indicates an improvement of crystallographic quality of the samples [AO]. As seen in fig. 2, for each heat treatment in $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$, the parameter c decrease, b is nearly constant for all systems but a increase with the ionic radius r(Ln^{3+}) from Ln = Eu to Sm then decrease for Nd leading to a decrease of the orthorhombicity ε = (b – a)/(b + a). This is due to the fact that the ionic radius of Eu^{3+}(0.95 Å), Sm^{3+}(0.965 Å) and Nd^{3+}(0.995 Å) ions are much larger than that of Y^{3+}(0.893 Å). For each Ln, the [AO] heat treatment increases b and c, but decreases a.

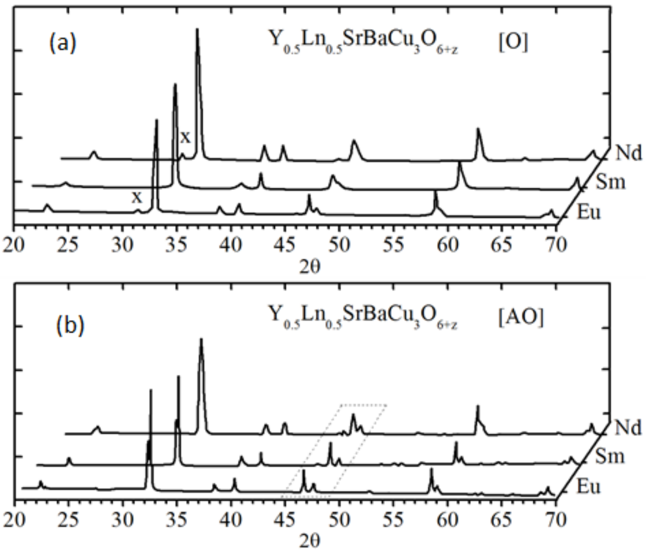

Fig. 1 XRD patterns for $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ as a function of ionic radius r(Ln^{3+}). (a) Samples [O], (b) samples [AO].

Whereas the volume V of the unit cell remain constant indicating a rearrangement of the unit cell (see Table. I). Also the [AO] heat treatment increase ε, for $Y_{0.5}Eu_{0.5}SrBaCu_3O_{6+z}$ from 5.872 10^{-3} to 8.355 10^{-3}, $Y_{0.5}Sm_{0.5}SrBaCu_3O_{6+z}$ from 4.033 10^{-3} to 6.638 10^{-3} and $Y_{0.5}Nd_{0.5}SrBaCu_3O_{6+z}$ from 3.913 10^{-3} to 7.174 10^{-3}.

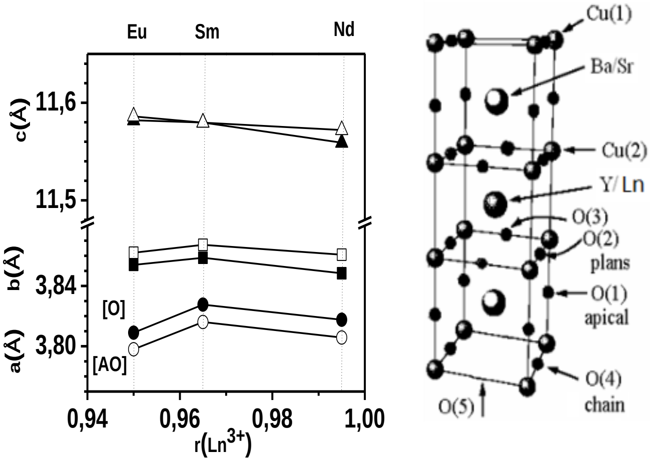

Fig. 2 Crystalline parameters as a function of the ionic radius r(Ln^{3+}). In the right the unit cell of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$.

In order to have an insight in the internal strains induced by the Ln substitution, we have calculated the interatomic distances d[Cu(1)–(Sr/Ba)]. An increase of this distance is observed with r(Ln^{3+}) indicating an increase of the stress introduced by the larger ionic radius replacing the smaller Y atom in the unit cell. For each r(Ln^{3+}), the [AO] heat treatment decreases the distance d[Cu(1) – (Sr/Ba)] (see Table. I).

Table. I : T_c and crystalline parameters of the $Y_{0.5}Ln_{0.5}BaSrCu_3O_{6+z}$ as function of heat treatment.

Ln	r(Ln)(Å)	h. Treat	a(Å)	b(Å)	c(Å)	V(Å^3)	ε*10^{-3}	T_c(K)	d[Cu(1)-(Sr/Ba)]
Eu	0.950	[O]	3.809	3.854	11.582	170.02	5.872	82.1	3.43811
		[AO]	3.798	3.862	11.586	169.94	8.355	82.5	3.43759
Sm	0.965	[O]	3.828	3.859	11.580	171.06	4.033	81.0	3.43582
		[AO]	3.816	3.867	11.580	170.88	6.638	82.0	3.43491
Nd	0.995	[O]	3.818	3.848	11.559	169.82	3.913	78.9	3.43502
		[AO]	3.806	3.861	11.572	170.05	7.174	80.5	3.43173

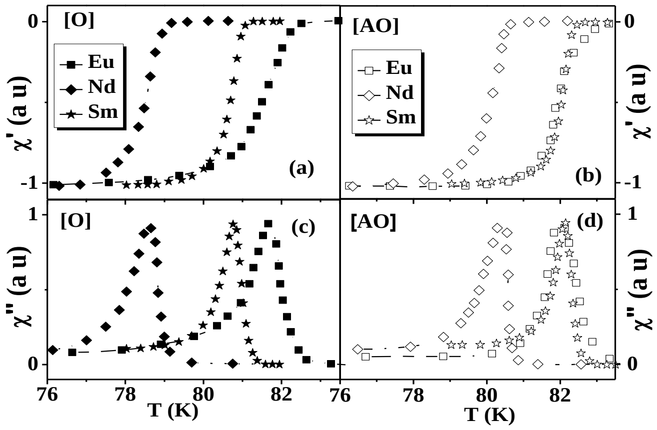

Fig. 3 χ' et χ" of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ as a function of the temperature and heat treatment; (a) Samples [O] (b) Samples [AO].

The temperature dependence of the real part of the susceptibility measurements (χ'), is plotted in Fig. 3 (a,b) for [O] and [AO] heat treatment. Since the same sample was used for both heat treatments, one can compare the diamagnetic shielding response (amplitude of χ'(T)) and note that screening current of the [AO] sample increased considerably compared to that of the [O] sample. The superconducting transition temperatures T_c, defined as the onset of diamagnetic transition, increases from 82.1 K [O], 80.98 K [O], and 78.86 K [O] to 82.47 K [AO], 82.02 K [AO] and 80.54 K [AO] for Eu-, Sm- and Nd- samples, respectively.

In Fig. 4 we shown the dependence of T_c versus r(Ln^{3+}) of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ systems. For each ionic size of Ln, the [AO] heat treatment increases T_c. For each heat treatment, when the ionic size r of the rare earth ion decreases T_c increases to a maximum for Ln = Eu. A maximum of increase in T_c of $\delta T_c = T_c[AO] - T_c[O] = 1.68$ K in sample Ln = Nd, and a minimum of $\delta T_c = T_c[AO] - T_c[O] = 0.37$ K in sample Ln = Eu were observed. So T_c depends in heat treatment and the ionic radius of the rare earth.

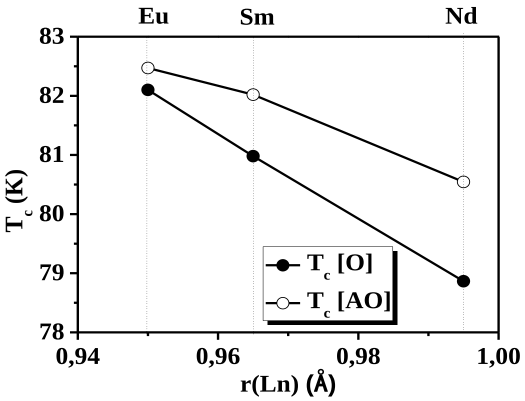

Fig. 4 T_c as a function of r(Ln^{3+}) and heat treatment of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd.

B. Imaginary part of the ac magnetic susceptibility and irreversibility line

According to the results of the imaginary part of the susceptibility measurements (χ") of our samples in (Fig. 3 (c,d)), we can see that χ" is very sensitive to heat treatment and the ionic radius size of Ln. The peak at T_p in the χ" reflects the intergranular critical current [20]. When the ionic radius of Ln increased, T_p shifted to low temperatures in the case of the samples [O]. For each Ln, T_p increased after [AO] heat treatment fallowing the increase of T_c.

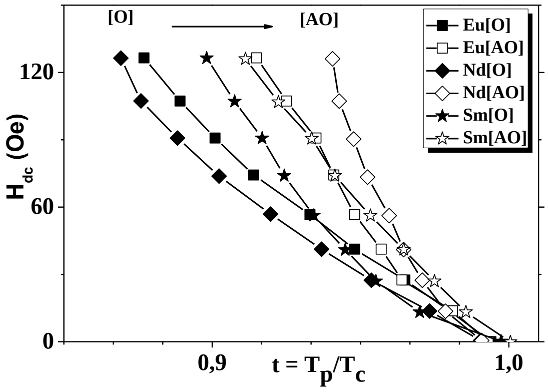

Fig. 5 H_{dc} as a function of t = T_p /T_c and heat treatment of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd.

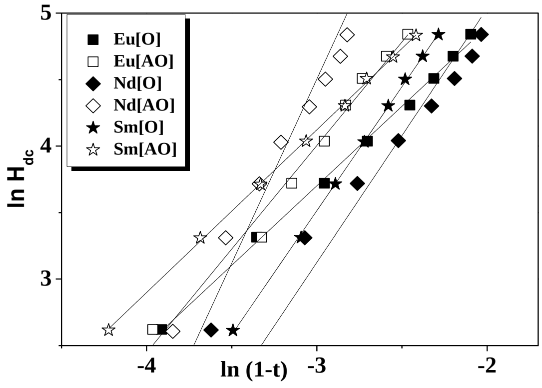

Fig. 6 ln(H_{dc}) as a function of ln(1 – t) and heat treatment for $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd.

Table. II Superconducting and magnetic parameters of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ as a function of r(Ln^{3+}) and heat treatment.

Ln	r(Ln)(Å)	h. Treat	T_p (K)	K'(Oe)	n
Eu	0.95	[O]	81.6	1463.8	1.19
		[AO]	81.9	5860.0	1.55
Sm	0.965	[O]	80.8	2423.1	1.22
		[AO]	81.2	9011.6	1.86
Nd	0.995	[O]	78.6	6982.0	1.90
		[AO]	80.0	366553.6	2.76

The magnetic field $H_{dc}(t)$ sets an upper limit to the irreversibility line (I.L.) marking the onset of dissipation and the region in which a superconductor can remain useful. In fact, when a static field H_{dc} is plotted as a function of $t = T_p/T_c$ (with $T_p = T_{irr}$) for the six samples in (fig. 5), an enhancement (an increase in the slope) of the irreversibility line was observed due to Argon heat treatment.

These results can be analyzed using the following equation $H_{dc} = K'(1\text{-}t)^n$ [21]. Straight line plots were obtained when Ln(H_{dc}) was plotted against Ln(1 – t) in (fig. 6). For each heat treatment, K' increases remarkably with r(ln^{3+}) in (fig. 7).

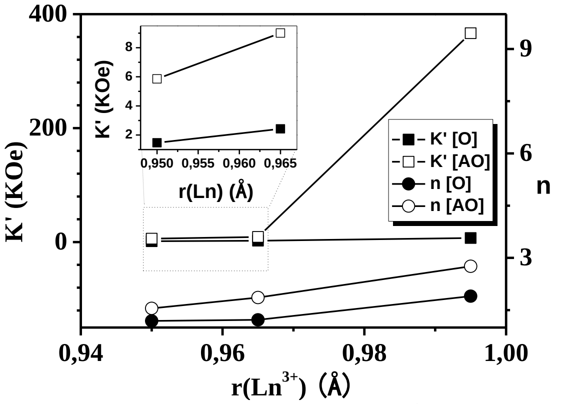

Fig. 7 The field K'as a function of the ionic size r(Ln^{3+}) and heat treatment of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd.

For each r(Ln^{3+}), the [AO] heat treatment increases the field K' and n indicating an improvement in the pinning properties. For example, the value of K' was estimated to be 6.982 KOe and 366.55 KOe respectively for the sample [O] and [AO] in $Y_{0.5}Nd_{0.5}SrBaCu_3O_{6+z}$ (Table. II). K' may be interpreted as the field necessary to reduce the intergranular critical current to zero in the limit of $T_p = 0$, and n define the type of the Josephson junction between the grains and intergrains in the superconductor.

IV. DISCUSSION

Our samples were prepared in 1 atm of oxygen. Further, the [AO] heat treatment did not sensibly change the total oxygen content 6+z, which was around 6.94±0.04 from our iodometry measurements but increased T_c. Thus the reason for this increase may lie in some other factor than z.

It is well-known that $YBa_2Cu_3O_{6+z}$ materials are orthorhombic superconducting and T_c is close to 92 K [22]. These materials are characterized by double $Cu(2)O_2$ layers (oriented along the a-b plane) responsible for carrying the supercurrent and Cu(1)O chains (along the b direction) which provide a charge reservoir for these planes [23] – [24].

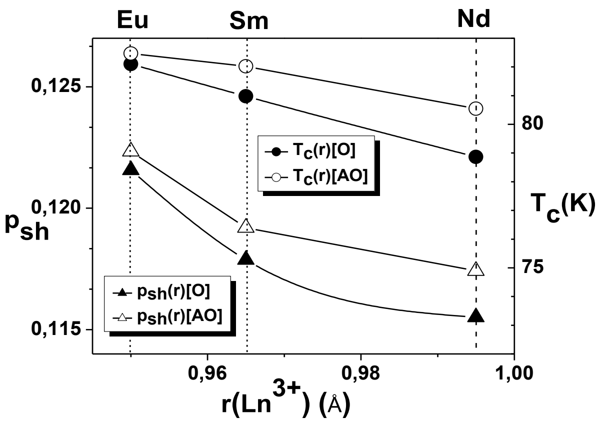

Fig. 8 Correlation between p_{sh} and T_c as a function of the ionic radius r(Ln^{3+}) and heat treatment of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd.

As seen in "table. I", the rare earths (Ln) substitution causes changes in the crystalline parameters a, b, and c, but keeps the orthorhombic character although there are minor changes in the orthorhombicity. This indicates that the ionic size r(Ln^{3+}) does not change the orthorhombic structure of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ systems. It was found that the argon heat treatment considerably increases the orthorhombicity, indicating an improvement of the structural and superconducting properties. G. Uimin et al. indicates that this increase of the orthorhombicity due to increase the order of oxygen in chain [25]. These authors indicated that the transfer of holes in the planes $Cu(2)O_2$ is strongly connected with the oxygen filling mechanism in basal plane on the O(4) and O(5) sites along b and a-axis respectively, as seen in the unit cell in the right of (fig. 2). This would lead to optimum superconducting properties and could account for the observed increase in T_c and the irreversibility line.

As seen in the left of (fig. 2), for each Ln, the [AO] heat treatment decrease the crystalline parameter a and increase b and c. This increase in parameter b leads to an increase of the number of oxygen atoms by chain (NOC) along the b-axis (increase of the anionic order in the basal plane). Indicating an improvement of transfer of holes from the Cu(1)-O chains (along the b direction) to the superconducting planes, via the apical oxygen O(1) (Fig. 2). This argument is justified by the decrease of d[Cu(1)-(Sr/Ba)] in (Fig. 9).

Therefore, the number of hole p_{sh} (Fig. 8) by $Cu(2)O_2$

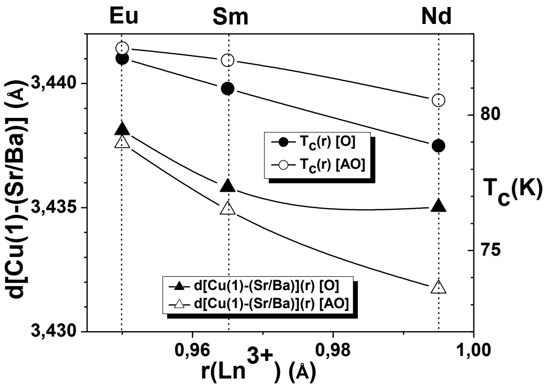

Fig. 9 Correlation between d[Cu(1)-(Sr/Ba)] and T_c as a function of the ionic radius r(Ln^{3+}) and heat treatment of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd

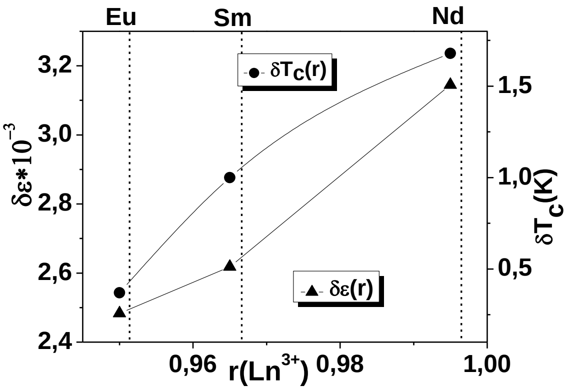

Fig. 10 Correlation between $\delta T_c = T_c[AO] - T_c[O]$ and $\delta\varepsilon = \varepsilon[AO] - \varepsilon[O]$ as a function of the ionic radius r(Ln^{3+}) and heat treatment of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ with Ln = Eu, Sm and Nd.

superconducting planes increases (deduced from the under saturation zone of the universal relation τ_c as a function of number p_{sh} of holes (with $\tau_c = T_c/T_c^{max}$) [26]) and T_c. For each r(Ln^{3+}), the [AO] heat treatment increases ε, T_c and decrease d[Cu(1)-(Sr/Ba)]. These results indicate a rearrangement of the same volume V of the unit cell and the enhancement of the charge transfer from chains to planes yielding to the increase of T_c.

When the Ln ion occupies Ba/Sr sites, the same amount of Ba/Sr cation is pushed in the Y sites (with Ln a trivalent ion). This increases the positive charge density around the Ba/Sr site and the attractive force with the oxygens. Therefore, the vacant oxygen sites O(4) have a greater chance of being filled.

On the other hand, Ba^{2+}/Sr^{2+} occupying the Y^{3+}/Ln^{3+} site reduces the intensity of the attractive force applied to the oxygen in the plane $Cu(2)O_2$. This increases the distortion angle of Cu(2)-O(2)-Cu(2) along the b-axis. Both changes in cation sites, increases b and decrease a after the heat treatment [AO]. This indicates the passage of oxygens in O(5) sites to the vacant sites O(4) along the b-axis. This increases the NOC and the oxygen chain order along b direction. This increase of NOC is responsible for transporting the negative charges of planes $Cu(2)O_2$ to chains Cu(1)-O via O(1), this increases the number of hole p_{sh} in superconductors plans. For each r(Ln^{3+}), the [AO] heat treatment increase p_{sh} indicating an improvement of superconducting properties in our systems.

The two arguments (cationic and anionic disorders) are justified here by the three remarkable correlations observed between T_c(r), the number p_{sh}(r) of holes by $Cu(2)O_2$ superconducting planes and d[Cu(1)-(Sr/Ba)] (r) in (fig. 8 and 9) respectively and on the other hand, between $\delta T_c(r) = T_c[AO] - T_c[O]$ and $\delta\varepsilon(r) = \varepsilon[AO] - \varepsilon[O]$ in (fig. 10). So the structural and superconducting properties are correlated with the effect of Argon heat treatment.

Hence we are tempted to believe that the changes (increase or decrease) observed in T_c, need not be related only to the ionic size of the rare earth but rather to a combination of several factors such as changes in the Cu(1)-O(1) distances, cationic and oxygen disorders, hole density etc.

V. CONCLUSIONS

To summarize, the effect of Ln substitution on the structural and superconducting properties of $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ system is analyzed. To determine the Structural properties, the results of the XRD measurements are analyzed using Rietveld refinement. The superconducting properties are analyzed using the AC magnetic susceptibility measurement approach. The following results are obtained:

- No obvious impurity phase after [AO] heat treatment in the XRD results. This result shows that there is an improvement of crystallographic quality of the samples [AO].
- For each heat treatment, T_c increases when the ionic size r(Ln^{3+}) decreases.
- For each ionic size of Ln, the [AO] heat treatment increases T_c. Regardless r(Ln^{3+}) and heat treatment, T_c increases when the ionic size r(Ln^{3+}) decreases and take a maximum for Ln = Eu. A maximum of increase in T_c of $\delta T_c = 1.68$ K in sample Ln = Nd, and the minimum of $\delta T_c = 0.37$ K in sample Ln = Eu were observed. So T_c depends in heat treatment and the ionic radius of the rare earth.
- The observed enhancement of the irreversibility lines in $Y_{0.5}Ln_{0.5}SrBaCu_3O_{6+z}$ after the Argon heat treatment were explained by the improvement of the quality of the grains, the intergranular coupling and the crystallographic quality of the [AO] samples. Three remarkable correlations were observed. So the structural and superconducting properties are correlated with the effect of Argon heat treatment.
- The [AO] heat treatment leads to an increase of number of oxygen per chain and decreases the distance between chains and the superconducting planes $Cu(2)O_2$ which increases the number of holes p_{sh}. This improve the transfer of charges via O(1), respectively, indicating that there is an improvement of superconducting properties in our systems.

All these results are the product of an interaction between the cationic disorder of Ln^{3+} on the site Sr/Ba along c axis and oxygen anion disorder in the basal plane. A combination of several factors such as the ionic size of the rare earth; decrease in d[Cu(1)-(Sr/Ba)]; increase in cationic and chain oxygen ordering; in-phase purity for the [AO] samples may account for the observed data.

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