Influence of Argon Heat Treatment on Structure, Critical Temperature, Magnetic Shielding and Irreversibility Line of $Ln(SrBa)Cu_3O_{6+z}$(Ln = Y, Eu)

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***Abstract*—We have studied the structural and superconducting properties of $Ln(SrBa)Cu_3O_{6+z}$(Ln= Y, Eu). Each of the two samples was submitted to two types of heat treatment: an annealing in oxygen [O] and a heat in argon followed by oxygen annealing [AO]. Our iodometry measurements indicate the same total oxygen constant 6 + z, which was around 6.95 ± 0.04 in each sample. The [AO] treatment increased the orthorhombicity $\varepsilon(*10^{-3})=(b-a)/(b+a)$from 8.23 to9.9 and from 3.1 to 6.97 in the samples with Ln= Y and Eu respectively., indicating a conservation of the orthorhombic structural phase. This was accompanied by an decrease of 1.3 K in critical temperature T_C to T_C[AO] = 81.7 K in the case of $YSrBaCu_3O_{6+z}$, while in the case of $EuSrBaCu_3O_{6+z}$, the T_C[O] = 81.1 K increase remarkably by 5.95 K to T_C[AO] = 86.7 K. Further, there was an enhancement of the irreversibility line whatever Ln. A combination of several factors such as the change of the ionic size of the rare earth Ln, its disorder on the (Sr, Ba) site, the chain oxygen ordering and increase in phase purity for the [AO] samples may qualitatively account for the observed data.**

Mots-clés : $LnSrBaCu_3O_{6+z}$; Heat treatments; Substitutions; XR diffraction ; AC magnetics susceptibility.

I. INTRODUCTION

Some of the technological applications of superconductivity include: the production of sensitive magnetometers based on SQUIDs, fast digital circuits (including those based on Josephson junctions and rapid single flux quantum technology), powerful superconducting electromagnets used in maglev trains, magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR) machines, magnetic confinement fusion reactors (tokamaks), the beam-steering and focusing magnets used in particle accelerators, electric motors and generators [1].

Extensive research efforts have been directed toward the study of high-temperature superconducting cuprates ever since its discovery in early 1986 [2].The microscopic theory of this phenomenon has not yet been elaborated. X ray diffraction (XRD) and AC. susceptibility ($\chi_{ac} = \chi' + i\chi''$) are very useful for characterizing the dynamics flux in high T_c superconductors (HTSC). A sharp decrease in the real part (χ'), just below the critical temperature Tc, is a consequence of diamagnetic shielding whereas in the imaginary part (χ''), the peak T_p represents AC losses.

It is well-know that the compound $YBa_2Cu_3O_{6+z}$ (with z ≈1) is superconducting below 92 K and characterized by double $Cu(2)O_2$ layers and Cu(1)O chains. The $Cu(2)O_2$ layers are oriented along the a-b plane responsible for carrying the supercurrent, while the Cu(1)O chains along the b direction provide a charge reservoir for these planes [3, 4]. The majority of the most requested searches for the superconductors compounds are those of the $LnBa_2Cu_3O_{6+z}$ systems (Ln = rare earth) which is stipulated by several reasons. On one hand, these compounds have a relatively high critical temperature Tc ≈ 90 K above the temperature of liquid nitrogen [5, 6]. On the other hand, the electric transport characteristics of these compounds can rather easily be varied by doping of the compound with substituting elements [7, 8] or varying the oxygen content [9, 10, 11]. The samples preparation has been made by several technologies with a given fault structure [12, 13] that is very useful for basic research.

Among the extensive work on the preparation and the study of the structural and superconducting properties of $La_{1+x}Ba_{2-x}Cu_3O_y$ (with $0 \leq x \leq 0.5$). Wada et al. [14], Izumi et al. [15] concluded that in order to have T_c maximal, this structure must have an ordered arrangement of La and Ba along c axis with an occupation factor of 0 and 1 for the oxygen at (1/2, 0, 0) and (0, 1/2, 0) sites, respectively.

We want to see if an isovalent substitution of Ba^{+2} by Sr^{+2} with smaller ionic radius can modify the results discussed above when Y^{+3} (r = 0.893 Å) is replaced by the rare earth Eu^{+3} (r = 0.95 Å) with bigger ionic radius. In the order to study the effect of the Y and Ba atomic plans on the superconductivity in $LnSrBaCu_3O_{6+z}$,we have studied the structural, superconducting and magnetic properties of the superconductor $EuBaSrCu_3O_{6+z}$ [16]. This compound when annealed in oxygen at 450°C showed an orthorhombic structure and a T_c of 81.1 K. When the same sample was heated in argon followed by oxygen annealing; we observed an increase both of orthorhombicity and T_c by 5.95 K. So T_c depends also on heat treatment.

In the case of $LnSrBaCu_3O_{6+z}$ (Ln = Y, Eu and z ~ 0.9) Wang et al. [17] and Badri et al. [18] obtained a quadratic structure and contradictory results (Table 1). To resolve these contradictions, we report here our results on sample preparation, X-ray diffraction and alternative magnetic susceptibility of $LnSrBaCu_3O_{6+z}$ (Ln = Y, Eu). In addition, we will examine the effect of the [AO] treatment, which has had a considerable influence on the structural, superconducting and magnetic properties of our samples.

II. EXPERIMENTAL TECHNICS

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. Ln_2O_3(Ln = Y, Eu), $SrCO_3$, $BaCO_3$ 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]. 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 [19].

Table 1. Lattice parameters a, c and Tc of $LnSrBaCu_3O_{6+z}$ (Ln =Y, Eu).

Ln	ref	a(Å)	c(Å)	T_c(K)
Y	[4]	3,789	11,563	83
	[5]	3,780	11,558	81.7
Eu	[4]	3,844	11,579	80
	[5]	3,845	11,590	60

III. RESULTS AND DISCUSSION

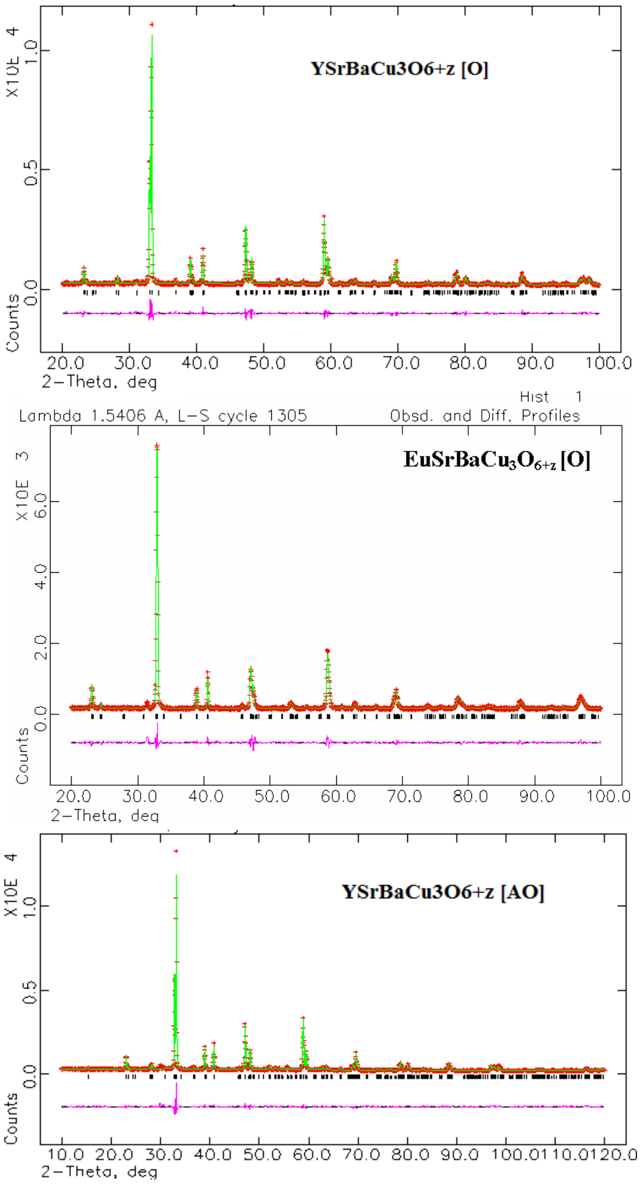
Superconducting transitions were checked by measuring both the real χ’ and the imaginary χ’’ parts of the AC susceptibility as a function of temperature in a field of 0.11 Oe and at a frequency of 1500 Hz.Then (χ’) and (χ”) were measured in a static field ($0<H_{dc}<150$ Oe) superimposed on the alternating field of 0.11 Oe.

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.

As example, the measured XRD patterns and refined with Rietveld refinement in the case of $LnSrBaCu_3O_{6+z}$ (Ln = Y, Eu) ([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 weak unidentified 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].

The [AO] treatment increased the orthorhombicity $\varepsilon(*10^{-3})=(b-a)/(b+a)$ from 8.23 to 9.9 and from 3.1 to 6.97 in the samples with Ln= Y and Eu respectively., indicating a conservation of the orthorhombic structural phase. This was accompanied by an decrease of 1.3 K in critical temperature T_C to T_C[AO] = 81.7 K in the case of $YSrBaCu_3O_{6+z}$, while in the case of $EuSrBaCu_3O_{6+z}$, the T_C[O] = 81.1 K increase remarkably by 5.95 K to T_C[AO] = 86.7 K (Table 2).

Further, there was an enhancement of their irreversibility line whatever Ln. The increase in T_c in $LnBa_2Cu_3O_{6+z}$ as a function of z is normally attributed to an increase in the orthorhombicity and to an increase in the oxygen ordering in the a–b plane. The argon heat treatment did not sensibly change the total content of oxygen, which was around 6.95±0.04 (Table 2), from our iodometry measurements but increase T_c. Thus, the reason for the increase in T_c may lie in some other factor than z. The exact reason for the change in the symmetry from orthorhombic to tetragonal – and vice versa depending on the heat treatment – and when Y is replaced by Eu in



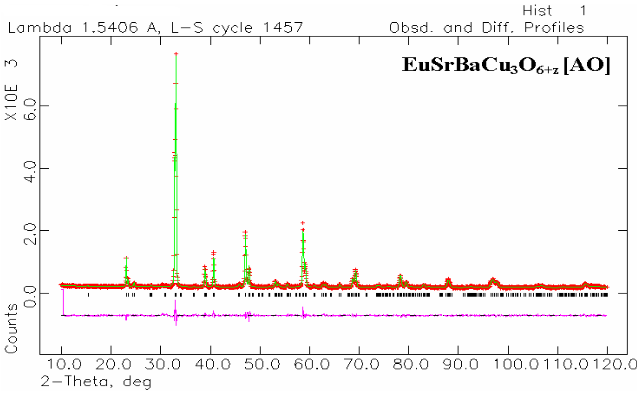


Fig.1: XRD pattern of $LnSrBaCu_3O_{6+z}$, (Ln = Y, Eu) observed, calculated with Rietveld refinement and difference profiles for sample [O] and sample [AO].

Table 2. Lattice and superconducting parameters of $LnSrBaCu_3O_{6+z}$ (Ln= Y, Eu) as a function of heat treatment.

Ln	h Treat	6+z (±0.4)	a(Å)	b(Å)	c(Å)	V(Å^3)	ε (*10^{-3})	T_c(K)	T_p(K)	ΔT_c(K)	ΔT_p(K)	n	K(Koe)	δK(Koe)
Y	[O]	6,96	3,789	3,852	11,563	168,73	8,23	83	82,9	0.41	0.3	3,22	27129,9	-26907,8
	[AO]	6,96	3,780	3,856	11,558	168,45	9,9	81.7	80,4	2.7	1.2	3,46	222,1	
Eu	[O]	6,946	3,831	3,855	11,607	171,2	3,1	81.1	80,1	2.71	2.29	1,41	1,6	30,1
	[AO]	6,95	3,813	3,867	11,604	171,11	6,97	87.05	86,7	1.26	0.9	1,72	31,7	

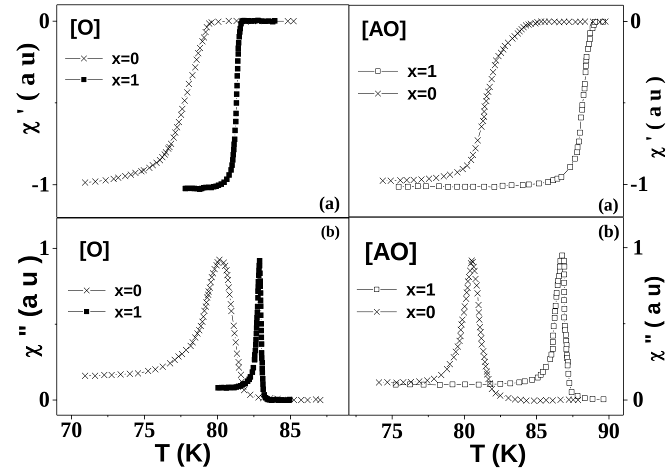


Fig. 2. (a)χ' and (b) χ'' of $Y_{1-x}Eu_xSrBaCu_3O_{6+z}$ (with: x = 0, 1) as a function of the temperature and heat treatment.

$YSrBaCu_3O_{6+z}$ is not known. We would like to suggest, however, that a tetragonal structure could be from an orthorhombic structure by rearranging the oxygen vacancies in the ab (basal) plane.

In the present case, the argon treatment seems to favor the orthorhombic symmetry. We propose, hence, that a rearrangement of oxygen atoms in the basal plane following the [AO] treatment would have caused an increase in the NOC (Number of Oxygen atoms per Chain) and this in turn would increase T_c.

When Eu ion occupies in Ba (or Sr) site, the same amount of Ba (or Sr) cation is pushed into Y site. Eu is a three-valence ion. It increases the positive charge density around Ba (or Sr) site and the attractive force with oxygen anion. As a result, oxygen vacancies O(4) along the b axis in the basal plane have higher chance to be filled. In the other hand, Ba^{2+} (or Sr^{2+}) in Y^{3+} site make decrease the attractive force with oxygen anion in Cu(2) plane. This increased the buckling angle Cu(2)–O(2)–Cu(2) along the b axis. The two changes of cation sites increase b and decrease a after the [AO] heat treatment (Table 2).This indicate the passage of some oxygen from O(5) sites to some vacant O(4) sites along b axis. So this increased ordering of chain oxygen along b direction (increase in the NOC). In addition c decreased by 0.013 Å. As result the Cu(1)-apical oxygen distance decreased. This could improve the transfer of charge between the chains and the Cu(2)-planes resulting in an increase in the hole density. Such an increase would lead to optimum superconducting properties and could account for the observed increase in T_c and irreversibility line.

In $Y(SrBa)Cu_3O_{6+z}$ the conservation of the orthorhombic structure can be explained by that a decreases and b increases slowly. The decrease of T_c by 1.3 K, after the [AO] heat treatment, can be explained by an increase of cationic order (along c) and anionic order in the basal plane. All these arguments are in agreement with the reduction of impurity in the samples [AO].

The real part χ 'of the alternative susceptibility measured under H_{ac} = 0.11 Oe as a function of temperature and heat treatment is shown on (Fig. 2); and on (Fig. 3) with 0 <H_{dc}<126.5Oe for $EuSrBaCu_3O_{6+z}$. Table 2 gives the critical temperature T_c of the transition from the superconducting state to the normal state. In the case $EuSrBaCu_3O_{6+z}$, T_c [O] = 87.05 K agrees with 80 K measured by Wang et al. [17] from resistivity but very high compared to T_c = 60 K observed by Badri et al. [18]. It is interesting to note that T_c increases remarkably by6 K to T_c [AO] = 87 K.

The imaginary part χ" (T, H_{dc}) of the alternative susceptibility as a function of the heat treatment for Ln = Eu is shown, as an example, on Fig. 3. They show that T_p move towards low temperatures, when H_{dc} increases, indicating the weakening of links between grains. This displacement is smaller in the sample [AO] than in the sample [O]. Table 2 shows that the T_p values of the χ" (T) peaks follow those of T_c. These two effects are also observed in the case of Ln = Y. However, when H is plotted as a function of $t = T_p/T_c$ in (Fig. 4 (a)), we observe an increase in the irreversibility line after the heat treatment [AO] in the case of $EuSrBaCu_3O_{6+z}$, whereas in the case of YSrBaCu3O6+z we observe a decrease in the irreversibility line due to the heat treatment [AO]. The plot of ln (H) as a function of ln (1 - t) (Fig. 4 (b)) leads to straight lines. Table 2 shows an increase of n ($1.4 \leq n \leq 3.5$) after the heat treatment [AO]. In the case of Ln = Eu, K[O] = 1573.41Oe increases remarkably to K[AO] = 31707.23Oe. K is interpreted as the field necessary to reduce the inter granular critical current at the limit of $T_p = 0$ K. Note that the argon heat treatment considerably increases the value of K indicating an improvement of the vortex shielding properties.

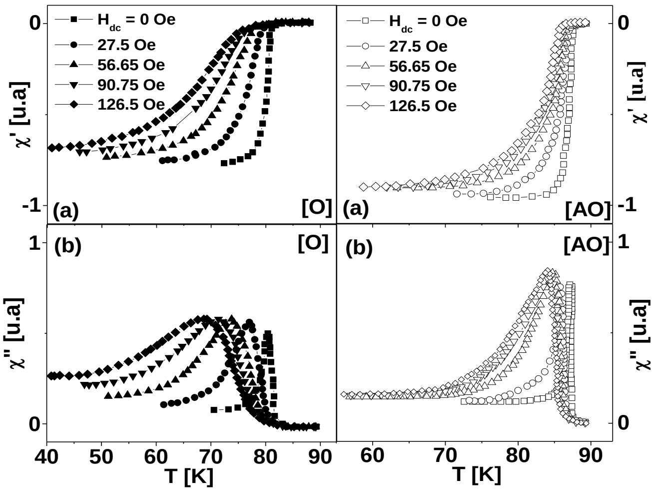


Fig. 3. (a) χ' and (b) χ'' of EuSrBaCu3O6+z as a function of temperature and the heat treatment at five different DC fields increasing form right to left: 0, 27.5, 56.7, 90.8 and 126.5 Oe.

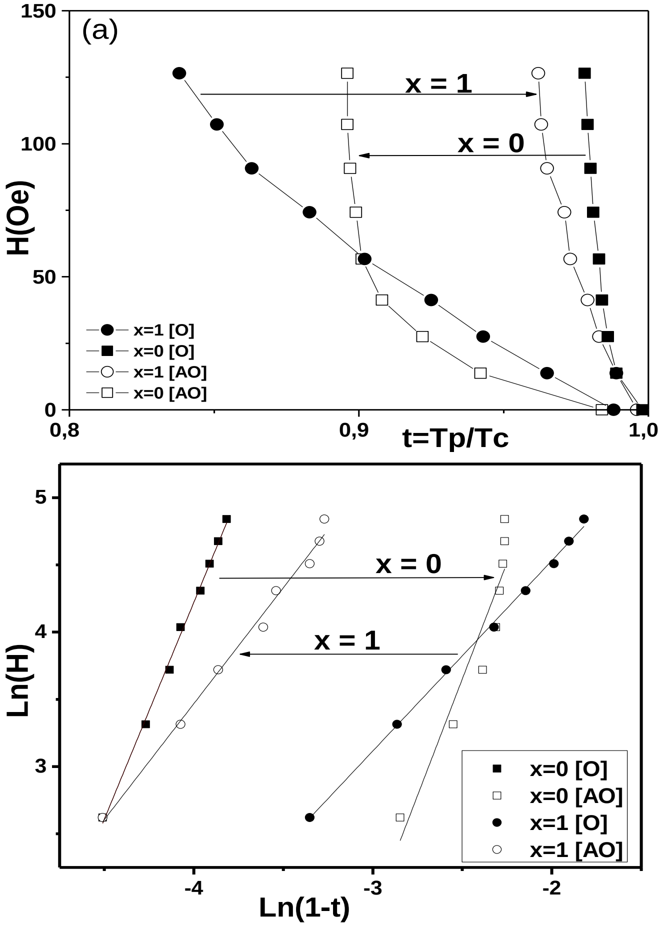


Fig. 4. (a) $t = T_p/T_c$ as a function of H, (b) ln(H) as a function of ln(1 - t): for the two samples Ln = Y and Eu as a function of heat treatment.

It is only the aspect – enhancement in the irreversibility line due to heat treatment – that we wanted to emphasize. Vanacken et al. [20] have measured the field-cooled and zero-field-cooled DC magnetization of $YBa_2Cu_3O_{6+z}$ as a function of z to establish the irreversibility line and analyzed their data using the relation $H = K(1 - t)^n$ [21]. They showed that n was independent of z but T_c and K (and also the orthorhombicity) increased with z indicating possibly the role played by an increase ordering of chain oxygen. Slight differences in oxygenation might also induce changes in Cu(1) – oxygen apical distance and T_c as was discussed elsewhere [22,23]. The observed increase in the irreversibility line may also be explained qualitatively by the factors discussed above.

Since the same sample was used for both heat treatments, one can compare the diamagnetic response and note that screening current of the [AO] sample increased considerably compared to that of the [O] sample(see for example the case Ln = Eu) in Fig. 2. (b).

Let us now look at the amplitude of the real part of the AC susceptibility in Fig. 3 which is nothing but the shielding effect S [24]. S was set arbitrarily equal to 1 for H_{dc} = 0 Oe. This was measured at three temperatures 70 K, 75 K and 80 K in the presence of an externally applied DC field H in Fig. 3. S represents the exclusion of magnetic flux by the sample in alternative dynamic mode. There was a remarkable Improvement in the shielding effect in the case of the samples [AO] at all $T < T_c$ and for any applied field H. For example in $EuSrBaCu_3O_{6+z}$ at T = 80 K , S at a field of 126.5 Oe was a factor of nearly nine higher in the case of the sample [AO] compared to that of the sample [0] (Fig.3). Further, the decrease in as a function of the field was much slower in the case of the sample [AO]. For example, at T = 80 K, the

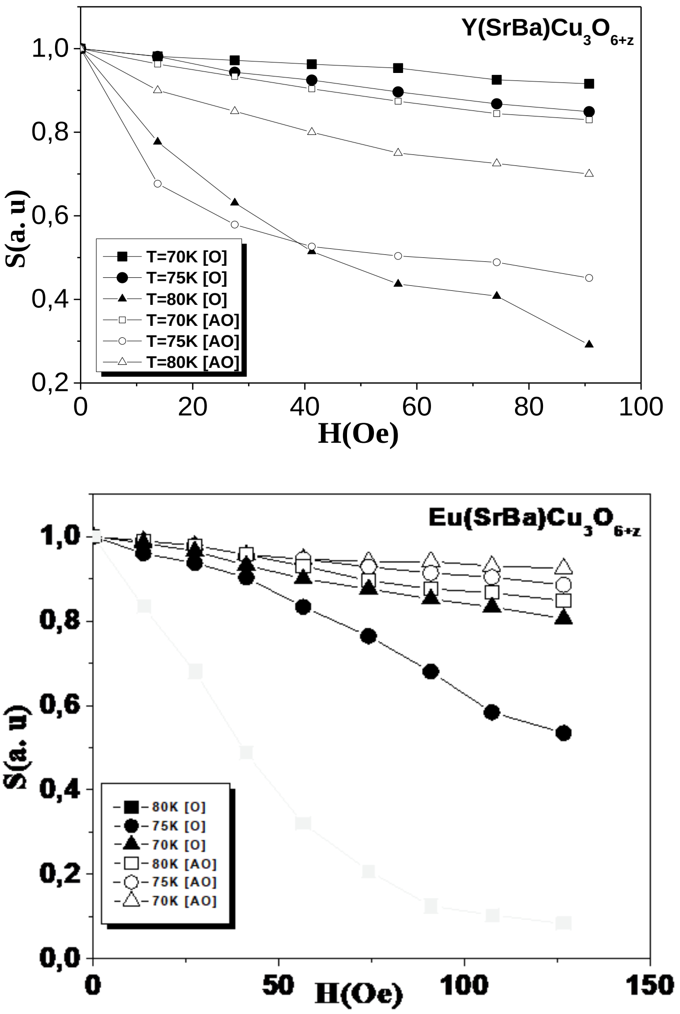


Fig. 5. Shielding effect S of $LnBaSrCu_3O_{6+z}$ (Ln = Y, Eu) as a function of the field H_{dc} and heat treatment at three different temperatures.

sample [AO] showed a decrease in S of about 10% as the field was increased from 0 to 126.5 Oe whereas the sample [0] showed a decrease of nearly 90%. It clearly shows an improvement of the quality of the grains and inter granular coupling in the sample [AO]. This effect is inversed in the sample Ln=Y.

We wish to make a brief comment on the relation between the ionic size of the rare earth Ln and T_c. For a given heat treatment [O] or [AO], the orthorhombicity, T_c and the irreversibility line (K) (except for Ln = Y) (Table 2 and Fig. 5) increase when the ionic size of the rare earth decreases. In the samples [O], the cationic and anionic disorders decrease with ionic size of the rare earth Ln. The [AO] heat treatment reduces these disorders and increase T_c. Hence we are tempted to believe that the changes 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)-apical oxygen distance, hole density, chain oxygen ordering and increase in phase purity for the [AO] sample.

A detailed NQR (Nuclear Quadrupole Resonance) study of our samples, extended to other superconductors with different rare earths, may be useful in discovering the role played by certain defects on the superconducting properties. The present studies indicate a simple heat treatment procedure to optimize superconducting properties.

IV. CONCLUSIONS

We have shown that the high critical temperature superconductors $Ln(SrBa)Cu_3O_{6+z}$ (Ln = Y, Eu) undergoing conventional oxygen heat treatment at 450°C crystallize with orthorhombic symmetry in disaccord with the tetragonal structure reported earlier by [17, 25]. The orthorhombicity, T_c and the irreversibility line increased the sample Ln = Y after [AO] heat treatment; whereas they decreases in Ln=Y. These results are due to interaction between the cationic disorder of Ln^{3+} at the (Sr/Ba) site and the anionic disorder of oxygen in the base plane. These disorders increases with the ionic radius of Ln and decrease after heat treatment [AO]. Our study indicates that a simple heat treatment process was able to optimize the structural and superconducting properties that should be investigated for other compounds of the $LnSrBaCu_3O_{6+z}$ system (where Ln = rare earth). We believe that these results will be useful for testing or improving some theoretical models of electronic structure and atomic disorder in view of the technological applications of high temperature superconductors.

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