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The Effect of Heat Treatment in the Superconducting $La_{1.84}Sr_{0.16}CuO_{4+\delta}$

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ABSTRACT

We synthesized the $La_{1.84}Sr_{0.16}CuO_{4+\delta}$ compounds ($\delta \approx 0.02$) using various heat treatments. The superconducting properties such as ac and dc magnetic susceptibility are largely correlated to the synthesis atmosphere. The sample annealed at higher temperatures in flowing O_2 has higher values of T_c and the Meissner volume fraction f, although the values of δ are almost the same for all the samples. We suppose that, in the case of the sample prepared in air, some of Sr atoms form dimers through the vacancies of apical oxygen in the (La, Sr)-O plane, which would lead to the heterogeneity of the Sr distribution causing the suppression of superconducting properties.

KEY WORDS: $La_{1.84}Sr_{0.16}CuO_{4+\delta}$, superconductivity, magnetic susceptibility, Meissner volume fraction, heat treatment

INTRODUCTION

The $La_{2-x}Sr_xCuO_{4+\delta}$ system exhibits the drastic phase change wiht the increase of x; antiferromagnetic→insulator-metal→superconducting transitions. We previously found that, in the light-doping regime ($0 \le x \le 0.02$), the rapid drop of the Néel temperature T_N has a close correlation with the hole concentration $h=x+2\delta$, where x and δ are Sr concentration and excess oxygen content, respectively, and therefore doped holes play the key role in destroying the Néel state [1]. In the further doping regime ($0.06 \le x \le 0.26$), the superconducting properties also depend on both x and δ. The value of T_c seems to shift systematically with x or δ, which have been discussed in terms of h [2, 3, 4].

However we found that annealing conditions largely affect the superconducting properties: powdered samples of $La_{1.84}Sr_{0.16}CuO_{4.02}$ ($x=0.16$, $\delta=0.02$) prepared by various heat treatments have different values of T_c and the Meissner volume fraction f, although the values of h are nearly the same for all samples ($h=0.20$). The change of the arrangement of the Sr and La ions in the La site depending on the annealing conditions is discussed as a possible origin of this behavior.

EXPERIMENTAL

The sample of $La_{1.84}Sr_{0.16}CuO_{4+\delta}$ was prepared by the solid-state reaction using high-purity powders of La_2O_3, $SrCO_3$ and CuO. The starting materials were well mixed, ground, pressed into pellets and preheated in air at 900 °C for 2 days. The resultant powder was heated at 1050 °C in air for 1 or 2 days with several intermediate grindings. Then the obtained powder (sample (A)) was separated into several parts and carried out various heat treatments as follows:

(1) annealing in flowing high purity O_2 gas (which we call the O_2 treatment) for 12 hours at 500 °C (B1), 600 °C (B2), 700 °C (B3) and 900 °C (B4).

(2) annealing first in flowing high purity N_2 gas (which we call the N_2 treatment) at 900 °C for 12 hours followed by the the O_2 treatment at 500 °C for 12 hours (C).

(3) the O_2 treatment for 1 hours at 500 °C (D1), 700 °C (D2), 750 °C (D3) and 900 °C (D4).

(4) the O_2 treatment at 750 °C for 10 hours (D2') and 100 hours (D2'').

Table. 1: Annealing conditions for $La_{1.84}Sr_{0.16}CuO_{4.02}$ prepared with various heat treatments

sample	atmosphere	annealed temperature	hold time	heating rate	cooling rate
A	air	1050 °C	48 hours		quench
B1	O_2	500	12	3 °C/min	1 °C/min
B2	O_2	600	12	3	1
B3	O_2	700	12	3	1
B4	O_2	900	12	3	1
C	N_2	900	12	3	5 (down to 500°C)
	O_2	500	12		1
D1	O_2	500	1	7	5
D2	O_2	700	1	7	5
D3	O_2	750	1	7	5
D4	O_2	900	1	7	5
D2'	O_2	700	10	7	5
D2''	O_2	700	100	7	5

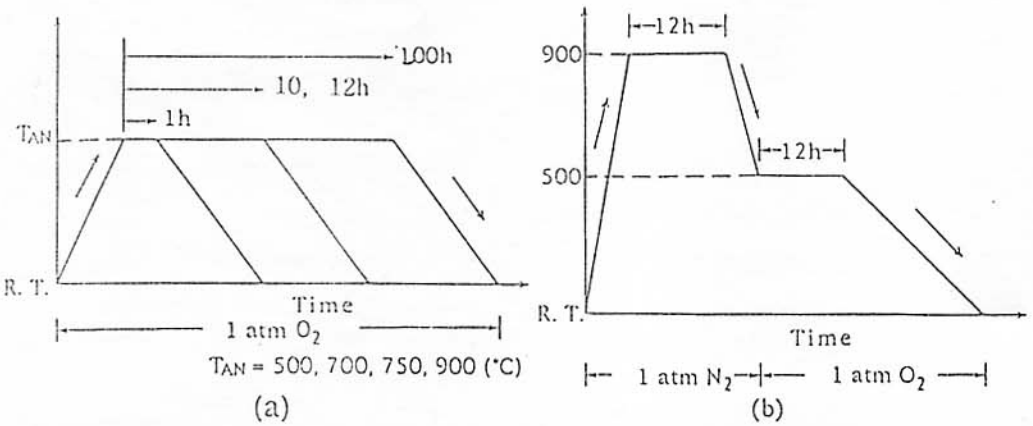

Fig. 1: Step diagrams of heat treatments. (a): Samples (B1-4), (D1-4), (D2') and (D2'') prepared by the O_2 treatment. (b): Sample (C) prepared by the O_2 treatment followed by the N_2 treatment.

The detailed procedure of heat treatments is summarized in Table 1 and step diagrams of heat treatments are shown in Fig. 1. The sample homogeneity was examined by means of X-ray powders diffraction using Cu-K_α. The coulometric titration technique with CuCl as a reductant was performed to determine the hole concentration h. The detailed procedure should be referred to those of Kurusu et al [5]. Temperature dependence of ac susceptibility was measured by using a conventional Hartshorn bridge method under the field of 10 mOe oscillating at a frequency of 270 Hz. The dc susceptibility was measured with a SQUID magnetmeter (Quantum Design: MPMS) in an applied magnetic field of 10 Oe.

RESULTS AND DISCUSSION

From the X-ray diffraction (XRD) analysis, all samples prepared were confirmed to be single phase with tetragonal symmetry and have nearly the same lattice parameters [6]. The hole concentration h determined by the coulometric titration method is 0.20±0.002 independent of heat treatment, leading the value of δ to be 0.02 (note that δ can be determined from the equation δ=(h-x)/2).

Figure 2 shows the temperature dependence of ac-χ for the samples (B1-4 and C). The inset of this figure is the enlarged plot near T_c. The values of T_c are 38.3, 37.7, 37.7, 37.2 and 35.9 K for the samples (B4), (B3), (B2), (B1) and (C), respectively. Generally, the sample annealed at higher temperature at the O_2 treatment shows good superconducting properties estimated by the values of f and T_c. The sample (B4) whose annealed temperature T_{AN} is the highest (900 °C) has the highest values of f and T_c=38.3 K. Furthermore, the superconductivity of the sample (C) is damaged, although the final heat treatment (the O_2 treatment) is the same as the one for the sample (B1). In Fig. 3, we show the temperature dependence of dc-χ for the samples (C, D1-4, D2' and D2''). One can find the behavior on the dc-χ data is similar to the one on the ac-χ data. The superconductivity gets better with increasing the heat treatment number as (D1)→(D4). The sample (D4) whose annealed temperature T_{AN} is the highest (=900 °C) has the highest values of f and T_c=38.3 K. The superconductivity tends to be improved by the O_2 treatment, while only the sample (C) performed the N_2 treatment before the O_2 treatment has smaller values of f and T_c than the starting compound of sample (A). In addition, we found an annealed time dependence on the superconductivity (compare the samples (D2), (D2') and (D2''), which are all annealed at 700 °C in flowing O2 gas). The value of f increases in order of increasing the time of annealing. From these results, we can conclude that annealing at high temperatures in the O_2 treatment process is indispensable in order to obtain a sample having good superconducting properties.

In order to elucidate the origin of the differences in T_c and f, we assume a model describing below: considering our previous report concluding that only the compound with x≈0.16 and δ≈0.0 shows intrinsic superconductivity, the sample (A) which is the starting powder of other samples should be heterogeneous due to oxygen vacancies at apical oxygen sites [2, 3]. Our Cu-NQR study suggests that, in the $La_{2-x}Sr_xCuO_{4+\delta}$ system, there would exist oxygen vacancies at apical site far from Sr atoms, indicating that some oxygen atoms are at the interstitial site [7]. Since the La ion has a larger valence than Sr ion by 1 and, thus, prefers highly oxygen-coordinated state, some Sr ions would form dimers through oxygen vacancies to hold the local charge neutrality, if there are any oxygen vacancies. The diagram of the Sr dimerization is shown in Fig. 4 (a). Oxidizing atmosphere (the O_2 treatment) would decrease the oxygen vacancies and lead a homogeneous distribution of Sr atoms (Fig. 4 (b)).

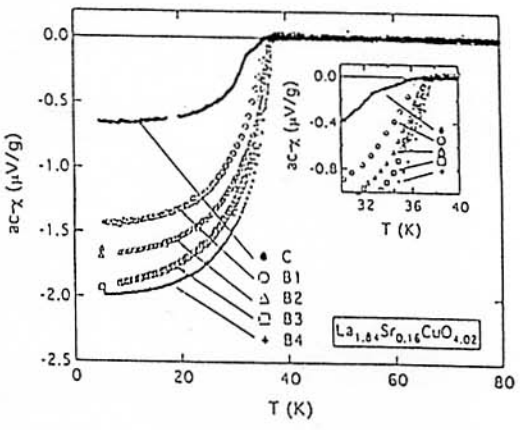

Fig. 2: Temperature dependence of ac-χ for the samples (B1-4) and (C). Since vertical axis is proportional to the induction voltage normalized by the sample weight, the values of difference samples can be compared. The inset is the enlarged plot of this figure near T_c.

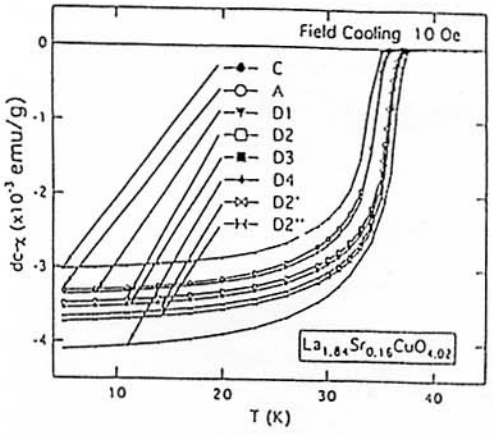

Fig. 3: Temperature dependence of dc-χ for the samples (A), (C), (D1-4), (D2') and (D2'').

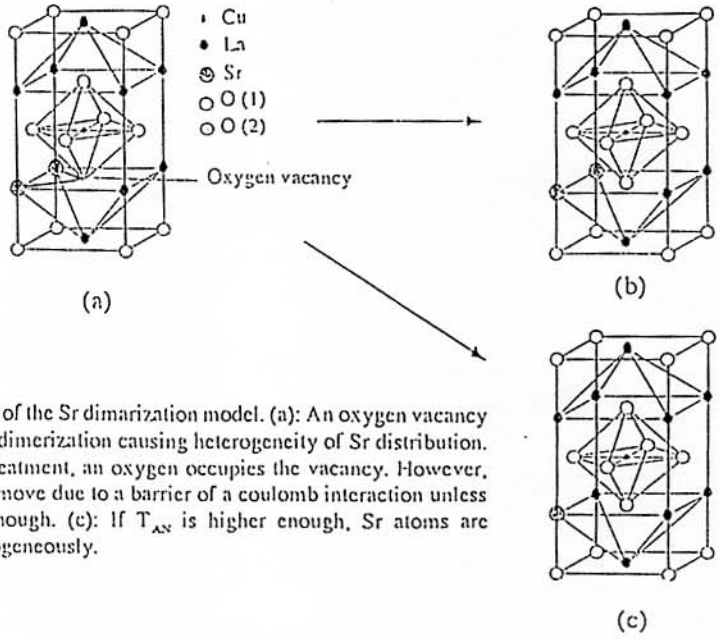

Fig. 4: Diagrams of the Sr dimarization model. (a): An oxygen vacancy introduce the Sr dimerization causing heterogeneity of Sr distribution. (b): By the O_2 treatment, an oxygen occupies the vacancy. However, Sr atom can not move due to a barrier of a coulomb interaction unless T_{AN} is higher enough. (c): If T_{AN} is higher enough, Sr atoms are distributed homogeneously.

which would improve the superconductivity. However, if T_{AN} is low at the process of the O_2 treatment, the distribution of Sr atoms would not become homogeneous completely, causing poor superconductivity, because for the Sr atoms it would be hard to move at lower temperature (Fig. 4 (c)). Therefore, the only samples (B4) and (D4) by the O_2 treatment at 900 °C would be homogeneous in the sense that doped holes are uniformly distributed. In the case of sample (C) having the lowest values of T_c and f, since P_{O_2} during the N_2 treatment is rather small, there would exist more oxygen vacancies than the case of sample (A) and the Sr atoms would be most heterogeneously distributed in the (La, Sr)-O plane. We could not observe any experimental XRD evidence indicating any phase separation implying that the heterogeneous distribution of Sr atoms may be small and could not be detectable by the XRD study. Similar effect of heat treatment can been seen in the $La_{1-x}Ba_{2-x}Cu_3O_y$ and $YBa_2(Cu_{1-x}M_x)_3O_y$ (M=Fe, Co) systems [8, 9].

In summery, we found that the superconducting properties for $La_{1.81}Sr_{0.16}CuO_{4.01}$ are largely affected by the synthesis atmosphere. The values of T_c and f increase with T_{AN} at the O_2 treatment process although the oxygen content is indepenent of heat treatments. We suppose when P_{O_2} is small, Sr dimers are formed through oxygen vacancies, which would lead to the heterogeneity of the Sr distribution causing the suppression of superconducting properties. Microscopic investigations are needed for further understanding of the physical behaviors of this system.

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