

Effect of Substituting a Fraction of Cu by La on the Transport Properties of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ Superconductor ($0 \leq x \leq 0.06$)

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Abstract

The effect of La doping on the transport properties and superconducting characterizations of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was investigated. High quality $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ superconductor was synthesized with La content of $x = 0.00, 0.02, 0.04$ and 0.06 . The structure and surface morphology were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. The best superconducting properties can be obtained for substitution of Cu by La concentration within a distinct range ($x = 0.02, 0.04$). The highest superconducting transition temperature T_c (≈ 90 K), sharpest transition to superconductivity ($\Delta T = 5$ K) and lowest electrical resistivity ($\rho = 9.2 \mu\Omega\cdot\text{cm}$) correspond to the composition with $x = 0.02$. Depression and degradation of the superconducting state as (x) increases to 0.06 were observed. Excess dopant of La ($x = 0.06$) results in a strong decoupling of chains and planes whereas optimal La doping ($x = 0.02, x = 0.04$) accumulates around the grain, beside the effect of hole filling within this range can adopt an alternate route to extensive oxygen anneal.

Keywords

Superconductors, X-Ray Diffraction, Transport Properties, Microstructure

1. Introduction

The search for high-temperature superconductivity and novel superconducting mechanisms is one of the most challenging tasks of condensed matter physicists as well as material scientists [1] [2] [3]. The studies on various substitutions in oxide superconducting systems have proven to be of great importance since changes in the critical transition temperature (T_c) are usually observed. For ex-

ample, the effects of non isovalence substitutions for (Y) in (YBCO) superconductors have attracted a great deal of attention in the past [4] [5]. Results show that, basically, such doping can vary the hole concentration in a controlled manner influencing the superconducting properties of the material obtained [6].

Doping of different ions at the copper sites in (YBCO) superconductors serves as a useful diagnostic probe to investigate the role of different copper sites in the occurrence of superconductivity in these superconductors [7] [8]. In almost all such cases, the destabilization of (YBCO) superconducting phases and consequently the degradation of superconductivity in these compounds have been determined at low substitution level. Also, the superconducting properties severely degraded by the substitution of transition elements in copper sites [9] [10], this suggesting that the principal component for superconductivity involves the (Cu-O) bonding.

In this work, toward the production of high quality superconducting material, a new composition $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ superconductor was proposed with La content ($x = 0.00, 0.02, 0.04$ and 0.06). The effect of substituting copper by (La) has been investigated. We present a study of the effect of (Cu) substitution by (La) on the transport properties of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$.

2. Experimental Work

Appropriate amounts of yttrium oxide, barium carbonate and copper oxide with starting composition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were mixed and ground in a marble mortar for one hour. The mixture was calcined in air at 910°C for 24 hours, with several intermittent grinding followed by oven cooling at 40°C per hour. The powders were reground and then pressed into tablets of ~ 13 mm in diameter and 4 mm in thickness using SPECAC press. The tablets were sintered at 910°C for 24 hours and slow cooled to room temperature at 40°C per hour.

Samples were prepared by using solid state reaction with four starting composition of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ for $x = 0.00, 0.02, 0.04$, and 0.06 . Samples were prepared by thoroughly mixing appropriate amounts of high purity ($\geq 99.99\%$) powders of (BaCO_3), (Y_2O_3), (La_2O_3), and (CuO) with starting compositions of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ for $x = 0.00, 0.02, 0.04$, and 0.06 . These powders were heated for 24 hours at 910°C with several intermittent grindings and oven cooled. The powders were then pressed into pellets with approximately 13 mm in diameter and 4 mm thick and heated at 910°C in air for another 24 hours followed by furnace cooling to room temperature at $\sim 40^\circ\text{C/hr}$.

The surface morphology of the sample was investigated by scanning electron microscopy (SEM) SU8000 series. X-ray diffractometer (Philips diffractometer (40 kV)) with Cu-K_α radiation ($\lambda = 0.15406$ nm) was used for XRD measurements. The resistance at various temperature of the samples was measured by four-point probe technique using a Keithley electrometer (model 6517B). Pasco 6560 interface was used for registering voltage, and current readings. The temperature was cooled down at a cooling rate of 40°C/hour and heated up with the same rate.

3. Results and Discussion

Structural characterization of the prepared composites was investigated using XRD and SEM measurements. **Figure 1** shows XRD patterns for $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ samples with different La concentration ($x = 0.00, 0.02, 0.04$ and 0.06). Judging from the observed reflexes, orthorhombic structure was identified in all the samples with no detectable impurity phases.

The surface morphology of the synthesized composites was investigated using SEM. SEM micrographs of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ with different (La) concentration ($x = 0.00, 0.02, 0.04$ and 0.06) is shown in **Figure 2**. The corresponding grain sizes for $x = 0.00, 0.02, 0.04$ and 0.06 , were $1.4, 1.6, 1.7,$ and $1.1 \mu\text{m}$ respectively (with an accuracy of $\varepsilon = \pm 0.1 \mu\text{m}$). Up to $x = 0.04$, a significant increment in the average grain size of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ as a result of increasing La concentration (x) was recorded. The decrease of the mean grain size at $x = 0.06$ is related to the un-uniformity of a wide variety of the mean grain size and multi-broken ones could be readily seen. This result of increasing the mean grain size reveals more uniformity of the whole grain growth process, more dense microstructure, and this agree with other reports [11].

The experimental results obtained by using resistivity measurement are presented in this work to show the effect of (Cu) substitution by (La) on the transport properties and T_c transition. Van der Pauw (four probe) method was used to determine the resistivity. The room temperature resistivity ρ was computed by:

$$\rho = \frac{\pi t}{\ln 2} \frac{V(cd)}{I(ab)}$$

where: t is the thickness of the sample, V_{cd} is the voltage between the points c and d and I_{ab} is the current through point a to b of the four probes. The resistance and temperature were recorded and plotted with a resistance versus temperature as shown in **Figure 3**. The measurements were extended over the temperature range from 300 K to 4.2 K . All the samples within (La) concentration range ($x = 0.00, 0.02, 0.04$ and 0.06) show metallic behavior ($\partial R/\partial T > 0$) before transition to superconducting state. Increasing (La) concentration x to 0.06 , the sample shows a semiconducting behavior ($\partial R/\partial T < 0$) before transition to superconductivity. The sample with $x = 0.06$, shows much higher resistance values and larger broad transition to superconductivity (summarized in **Table 1**). Regarding to the metallic behavior for lower La content ($x = 0.00, 0.02, 0.04$ and 0.06) and the semiconducting behavior at $x = 0.06$ which was investigated. It is verified that the superconducting properties is established up to $x = 0.04$ and the quality of the composites decays at $x = 0.06$. Furthermore, highest $T_c \approx 90 \text{ K}$ and sharpest transition to superconductivity ($\approx 5 \text{ K}$) is seen for the doped samples with (La) range ($x = 0.00, 0.02, 0.04$ and 0.06).

Figure 4, shows the concentration dependence of the onset transition temperature and the critical transition temperature $T_{c\text{-zero}}$ of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ composites. It is observed that the highest $T_{c\text{-onset}}$ corresponds to the samples of x

= 0.02 and 0.04. The highest T_c is observed in the samples with La concentration in the range of $x = 0.02, 0.04$ and the lowest T_c value is seen for the sample with ($x = 0.06$). Such behavior confirms the superconducting behavior and compatible with the above mentioned resistance measurements.

The variation of the broadening of the superconducting transition width (ΔT) with different La concentration of the prepared samples is shown in **Figure 5**. It can be clearly seen that the sharpest transition corresponds to the samples within La concentration range of ($x = 0.00, 0.02, \text{ and } 0.04$) which reinforce the preceding results.

Figure 6 shows the concentration dependence of electrical resistivity (ρ). It was found that, the lowest resistivity value ($\rho = 9.2 \mu\Omega\cdot\text{cm}$) corresponds to the sample of (La) concentration of $x = 0.02$, and the highest value ($\rho = 4.3 \times 10^{-5} \Omega\cdot\text{cm}$) corresponds to (La) concentration of $x = 0.06$. One can conclude that, the best superconducting properties corresponds to the samples of (La) concentration $x = 0.02$ and 0.04 . Kini *et al.* reported that the reduction in copper valence is evident from decrease in resistivity (ρ) with increasing the dopant content [12]. Within La concentration $x = 0.02$, it is evident that the dominant charge neutralizing mechanism is the intake of oxygen into lattice as reported previously [12]. The rise of (La) concentration $x = 0.02$ up to 0.06 results in an increase of resistivity values (ρ). This increase of the resistivity is in agreement with Llonca *et al.* [13]. They reported a model to better understanding of the involved carrier scattering mechanisms for the effect of the partial substitution of (Cu) by (Zn). Their model has been interpreted in the percolative phase separation theory. In addition, it has been reported that the dual role of substituting (Cu) by (Co) is to enhance T_c at low concentration and depressing it in higher dopant concentration [14].

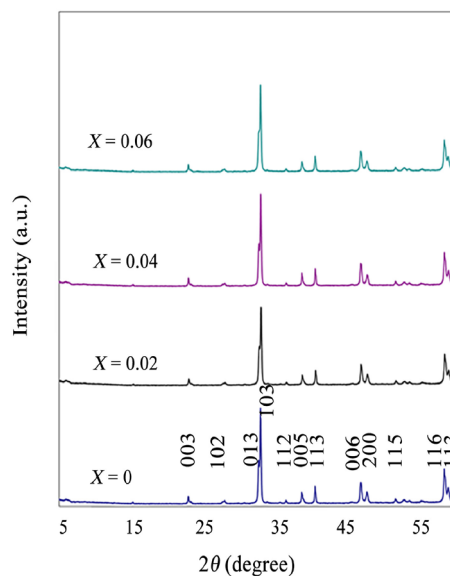


Figure 1. XRD for $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ composites with different La content ($x = 0, 0.02, 0.04$ and 0.06).

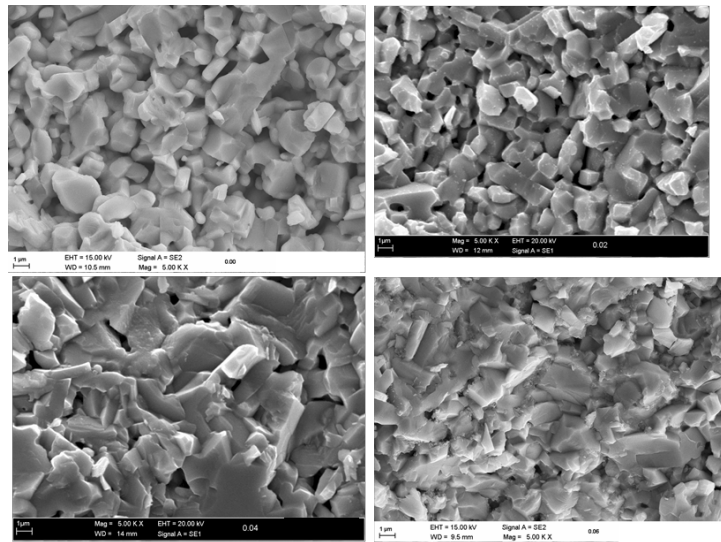


Figure 2. SEM micrographs of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ composite with $x = 0, 0.2, 0.04$ and 0.06 .

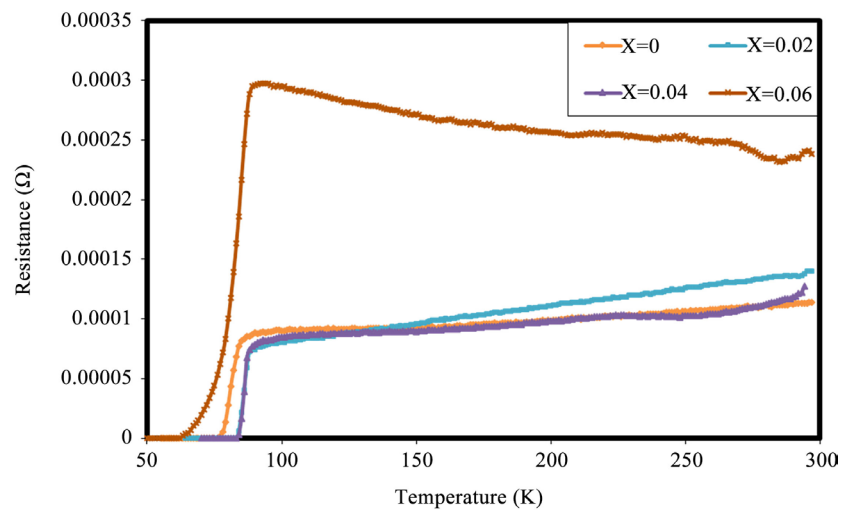


Figure 3. The variation of resistance with temperature for $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ with ($x = 0, 0.02, 0.04$ and 0.06).

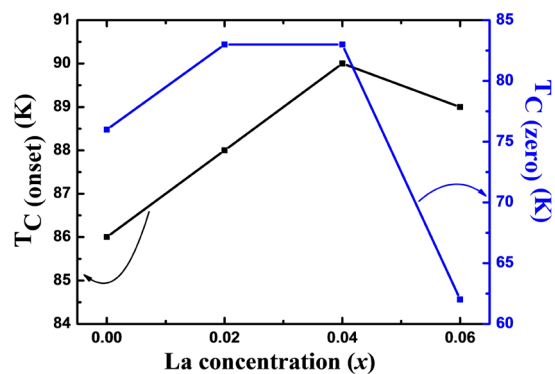


Figure 4. The concentration dependence of the onset transition temperature $T_{c\text{-onset}}$ and zero transition temperature $T_{c\text{-zero}}$ of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$

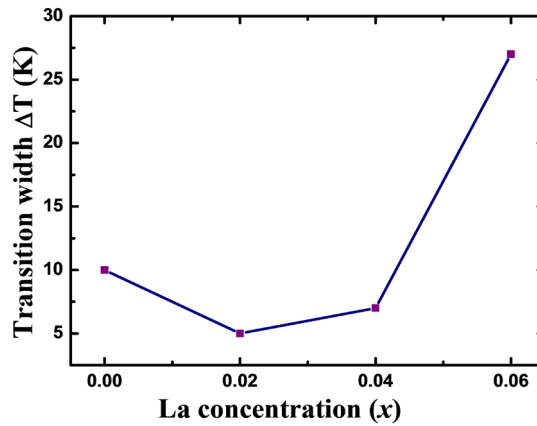


Figure 5. The variation of the transition width (ΔT) with La content x of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$.

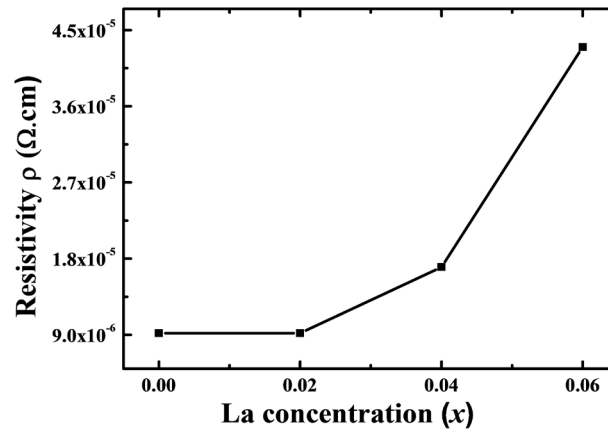


Figure 6. Electrical resistivity of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ versus La concentration.

Table 1. Onset temperature ($T_{c\text{-onset}}$), zero resistance temperature ($T_{c\text{-zero}}$), resistivity (ρ) at 300 K, transition width (ΔT_c) and the normal state of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$.

(La) cont. (x)	$T_{c\text{-onset}}$ (K)	$T_{c\text{-zero}}$ (K)	ΔT_c (K)	ρ at 300 K (Ω)	State
0	86	76	10	1.1×10^{-5}	Metallic
0.02	88	83	5	9.2×10^{-6}	Metallic
0.04	90	83	7	1.7×10^{-5}	Metallic
0.06	89	62	27	4.3×10^{-5}	Semiconductor

The previous reports agree completely with the present results and can be understood on the basis of the apex oxygen model [14] and structural studies [15] [16] in doped YBCO. It was indicated that the most sensitive change of crystal structure on doping is related to apical oxygen. Several theoretical models emphasize the significance of this oxygen in the occurrence of superconductivity [14].

4. Conclusion

The study of transport properties of $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$ indicated that the best superconducting properties can be obtained for substitution of (Cu) by (La) concentration within the range ($x = 0.02$, and 0.04). The highest T_c (≈ 90 K), sharpest transition to superconductivity ($\Delta T = 5$ K) and lowest electrical resistivity ($\rho = 9.2 \mu\Omega\text{-cm}$) are corresponding to La contents of $x = 0.02$ and 0.04 in $\text{YBa}_2(\text{Cu}_{1-x}\text{La}_x)_3\text{O}_{7-\delta}$. The highest T_c was attributed to more holes, more carrier concentration and more cooper pairs. Therefore, one can conclude that excess dopant of La ($x = 0.06$) results in a strong decoupling of chains and planes whereas optimal (La) doping ($x = 0.02$, and $x = 0.04$) can be adopted an alternate route to extensive oxygen anneal and may work as a catalyst which may cause partial melting and enhances all the superconducting properties.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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