Synthesis and characterization of La$_{2-y}$Y$_{y}$CuO$_4$ with T'-structure

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Abstract. Superconductivity is a phenomenon when the resistivity becomes zero below the critical temperature ($T_c$). The appearance of superconductivity in undoped bulk samples of T'-La$_{1.8-x}$Eu$_{0.2}$M$_x$CuO$_4$ ($M$ = Sr, Ca; $x$ = 0.05, 0.10, 0.15) has altered the existing phase diagram in superconducting cuprates and raised big questions about the mechanism of superconductivity. Here, new materials of T'-La$_{2-y}$Y$_{y}$CuO$_4$ with $y$ = 0.05, 0.10, 0.15 have been synthesized by the low-temperature synthesis method in order to grow undoped superconductors with the single phase of the T'-structure. The powder x-ray diffraction analysis was performed to identify of the crystal structure, while magnetic susceptibility measurements were carried out using a SQUID magnetometer at low temperature down to 2 K. It has been found that the T'-structure is stabilized when it was annealed at 500 – 600°C. The c-axis length decreases with increasing Yttrium-concentration. For $y$ = 0.10, the single phase of the T'-structure was obtained by the oxidation annealing at 300°C and the succeeding reduction annealing at 500°C for 24 hours. From magnetic susceptibility measurements, it has been found that no trace superconductivity is observed in all samples, which is probably due to the remaining excess oxygen suppressing the appearance of superconductivity in the sample.

1. Introduction

The mother compounds of high-$T_c$ cuprates have long been considered to be antiferromagnetic insulators. The superconductivity appears through hole and electron doping into insulating mother compounds of Ln$_2$CuO$_4$ (Ln: lanthanide element) with the K$_2$NiF$_4$-type (so-called T-type) and Nd$_2$CuO$_4$-type (so-called T'-type) structures, respectively. There are a lot of studies reported on the crystal growth, magnetic and transport properties of T-type samples [1-3], which are conterary to those of T'-type samples [4].

In adequately reduced thin films of T'-Nd$_{2-x}$Ce$_x$CuO$_4$, however, it has been reported that superconductivity appears in a wide range of $x$ and even in the undoped mother compound of $x$ = 0 [5]. Moreover, Takamatsu et al. have succeeded in synthesizing undoped and hole-doped bulk samples of T'-La$_{1.8-x}$Eu$_{0.2}$M$_x$CuO$_4$ ($M$ = Sr, Ca; $x$ = 0, 0.05, 0.10) by the low-temperature synthesis method [6, 7]. These surprising results suggest a new phase diagram of superconductivity and attract great interest on the mechanism of emerging superconductivity in T'-Ln$_2$CuO$_4$.

The hole and electron doping are usually achieved by the partial substitution of Sr$^{2+}$ and Ce$^{4+}$ for Ln$^{3+}$, respectively. The Ionic radius of Ln in Ln$_2$CuO$_4$ has a big deal to decide the crystal structure. It
prefers to the T'-structure instead of the T-structure when the ionic radius is small [8]. Furthermore, in the T'-La$_{1.8}$Eu$_{0.2}$CuO$_4$ (T'-LECO) system, however, it has been known that Ce cannot be substituted for La because of the production of a stable second phase of T'-Eu$_2$CeCuO$_4$. Where the ECCO itself, has been reported has the T' tetragonal structure [9]. Therefore, in order to investigate both hole and electron doping dependences of the superconductivity around $x = 0$ using the same T'-La$_2$CuO$_4$ system, we have chosen T'-La$_{2-x}$Y$_x$M$_x$CuO$_4$ ($M = $ Sr, Ce), in which Y is used instead of Eu. In the present work, accordingly, we have tried to prepare superconducting bulk samples of the undoped mother compound of T'-La$_{2-x}$Y$_x$CuO$_4$ (T'-LYCO).

2. Experiments
First, samples of T-LYCO with $y = 0.05$, 0.10, 0.15 were prepared by the conventional solid-state reaction method. The raw materials were mixed using a ball mill and sintered in O$_2$ gas flow at 1050°C for 24 hours.

Next, the samples of T-LYCO were mixed with reductant CaH$_2$ in a molar ratio of T-LYCO:CaH$_2$ = 1:2 in an argon-filled glove box. Then, the mixtures were sealed in an evacuated Pyrex tube, heated at 275°C for 24 hours, and washed with saturated NH$_4$Cl in anhydrous ethanol, so that samples of La$_{2-x}$Y$_x$CuO$_{3.5}$ with the Nd$_x$CuO$_y$-type (so-called N-type) structure were prepared. Then, the obtained samples of N-La$_{2-x}$Y$_x$CuO$_{3.5}$ were oxidized at 200 – 400°C to obtain samples of T'-LYCO. Since the obtained samples of T'-LYCO included excess oxygen, they were reduced in vacuum at various temperatures to remove the excess oxygen. All the samples were characterized by the powder X-ray diffraction (XRD) analysis at room temperature. Magnetic susceptibility measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and Discussion
From the powder XRD analysis, as shown in figure 1, it has been found that single-phase samples of T-LYCO with $y = 0.05$ and 0.10 are obtained by the conventional solid-state reaction method, while there remains a small amount of Y$_2$O$_3$ for $y = 0.15$. The peak width of samples sintered at 1050°C is found to be sharp, indicating T-LYCO samples sintered at 1050°C are of high crystalline quality. This condition is reasonable. The T-type structure is stable at high temperatures, because the size mismatch between the larger CuO$_2$ layer and the smaller LaO layer due to the substitution of Y$^{3+}$ smaller than La$^{3+}$ is relaxed at high temperatures owing to the thermal expansion of the ionic La-O bond larger than that of the covalent Cu-O bond [10].

![Figure 1](image-url)

**Figure 1.** Powder XRD patterns of T-La$_{2-y}$Y$_y$CuO$_4$ samples with $y = 0.05$, 0.10, 0.15 heated in O$_2$ at 1050°C for 24 hours.

After the reduction using CaH$_2$, it has been found that single-phase samples of N-La$_{2-y}$Y$_y$CuO$_{3.5}$ with $y = 0.05$ are obtained, while there remains a small amount of Y$_2$O$_3$ for $y = 0.10$ and 0.15. Figure 2
shows the powder XRD patterns of T'-LYCO samples \( (y = 0.05, 0.10, 0.15) \). All of the pattern can be indexed as the T'-structure. It is found that T'-LYCO is obtained by the oxidation at 200 - 400\(^\circ\)C. These results reveal that as-grown samples of T'-LYCO with \( y = 0.05 \) are of the single phase for all oxidation temperatures. Next, with increasing Y-concentration, it is found that a small \( \text{Y}_2\text{O}_3 \) peak appears for both samples with \( y = 0.10 \) and 0.15. Furthermore, an unknown peak is also observed for both sample with \( y = 0.10 \) and 0.15 around 25°.

![Figure 2](image_url)

**Figure 2.** Powder XRD patterns of T'-La\(_{2-y}\)Y\(_{y}\)CuO\(_4\) samples obtained by the reaction between T-La\(_{2-y}\)Y\(_{y}\)CuO\(_4\) and CaH\(_2\) and the oxidation at various temperatures. (a) \( y = 0.05 \), (b) \( y = 0.10 \), (c) \( y = 0.15 \). \( T_{ox} \) indicates the oxidation temperature.

Figure 3 shows the powder XRD pattern of the samples obtained by the reduction annealing. After the reduction annealing at various temperatures in vacuum for 24 hours for the removal of excess oxygen, it is found that single-phase samples of T'-LYCO are obtained only by the reduction annealing at 500\(^\circ\)C and 550\(^\circ\)C. While \( \text{Y}_2\text{O}_3 \) and \( \text{La}_2\text{O}_3 \) are found to appear together with T'-LYCO with increase of the Y-concentration and the reduction annealing temperature above 600\(^\circ\)C, respectively. This may be due to the decomposition on the surface of crystalline grains.

![Figure 3](image_url)

**Figure 3.** Powder XRD patterns of T'-La\(_{2-y}\)Y\(_{y}\)CuO\(_4\) samples oxidized at 300\(^\circ\)C and reduced at various temperatures. (a) \( y = 0.05 \), (b) \( y = 0.10 \), (c) \( y = 0.15 \). \( T_{red} \) indicates the reduction annealing temperature.
The T'-structure has been found to be broken with increasing reduction annealing temperature $T_{\text{red}}$, indicating that the T'-structure is unstable at high temperatures on account of the removal of indispensable oxygen by the strong reduction. The broken sample can be confirmed visually, because a part of the powder sample turns into brown. This is consistent with the former report [11] where it has been described that T'-$La_2CuO_4$ is stable only below 600°C.

Figure 4 shows the $y$ dependence of the $c$-axis length of T'-LYCO samples reduced on various conditions. It is found that the $c$-axis length slightly decrease with increasing $y$. This is reasonable, because the ionic radius of $Y^{3+}$ (0.92 Å) is smaller than that of La$^{3+}$ (1.16 Å). However, in the case of samples of $y = 0.15$, the $c$-axis lengths tend to be larger than those of $y = 0.10$. This may be caused by the presence of impurities of $Y_2O_3$ for $y = 0.15$.

![Figure 4. Yttrium-concentration dependence of the c-axis length of T'-La$_{2-y}$Y$_y$CuO$_4$ samples oxidized in O$_2$ at 300°C for 12 hours and reduced at various temperatures.](image)

Figure 5 shows the temperature dependence of the magnetic susceptibility in a magnetic field of 10 Oe for T'-La$_{2-y}$Y$_y$CuO$_4$ samples ($y = 0.05$, 0.10, 0.15) reduced at 500°C and 550°C. The inset shows the temperature dependence of the magnetic susceptibility of superconducting T'-La$_{1.8}$Eu$_{0.2}$CuO$_4$ for reference [6].

Figure 5 shows the temperature dependence of the magnetic susceptibility of T'-LYCO. It is found that no superconductivity appears in any reduced samples. The magnetic susceptibility of superconducting T'-LECO is also shown in the inset of figure 5 for reference. It is known that
undoped superconductivity is observed in samples with little excess oxygen whose $c$-axis length is not too large [6]. Meanwhile, the present result shows that the $c$-axis length of $T'$-LYCO is ~12.54 Å and longer than that of superconducting $T'$-LECO (12.458 Å), suggesting that there remains excess oxygen yet in $T'$-LYCO samples and that the excess oxygen suppresses the appearance of superconductivity.

4. Conclusions
LYCO ($y = 0.05, 0.10, 0.15$) samples with the $T'$-structures have successfully been synthesized by the low-temperature synthesis method at various temperatures below 600°C. The $c$-axis length decreases with increasing Yttrium-concentration. For $y = 0.10$, the single-phase sample of the $T'$-structure has been obtained by the oxidation annealing at 300°C and the succeeding reduction annealing at 500°C for 24 hours, with the $c$-axis length of 12.53 Å. However, no superconductivity has been observed in all the samples which is probably due to the existence of excess oxygen in the samples.

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