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Superconductivity in bulk T′-(La,Sm)$_2$CuO$_4$ prepared via a molten alkaline hydroxide route

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ABSTRACT

We have synthesized La$_{2-x}$Sm$_x$CuO$_4$ ($0 \leqslant x \leqslant 2.0$) with the Nd$_2CuO_4$ structure via a molten alkaline hydroxide route at temperatures as low as 400–480 °C. After reduction heat treatment in vacuum at 600–750 °C for removal of excess oxygen atoms at the interstitial apical site, superconductivity with T_c = 20–24 K was observed in the samples with x = 0.05–1.0. The superconducting volume fraction is nearly 100% for x = 0.3–0.7. Our results demonstrate that La$_{2-x}$Sm$_x$CuO$_4$ with no nominal carrier doping is a bulk superconductor.

1. Introduction

It has been a consensus for a long time that the parent compounds of high-T_c cuprates are, universally, a Mott–Hubbard insulator (more strictly, charge-transfer insulator) and that high-T_c superconductivity develops only after *p*-type doping or *n*-type doping. The cuprates with the Nd$_2$CuO$_4$ (abbreviated as T′) structure have been categorized as "*n*-type" superconductors since *n*-type doping via Ce^{4+} substitution for RE^{3+} has been believed to be prerequisite to achieving superconductivity [1,2]. However Ce doping alone does not achieve superconductivity in T′ cuprates and oxygen reduction is also prerequisite for superconductivity. The purpose of oxygen reduction is not further electron doping by introducing oxygen vacancies but removal of excess oxygen atoms at the interstitial apical site (O$_{ap}$) [3–11]. In T′ cuprates, a fair amount of excess oxygen atoms ($\delta \sim 0.1$ in RE_2CuO$_{4+\delta}$, *RE*: rare-earth element) occupy the O$_{ap}$ site in as-grown bulk samples prepared in ambient atmosphere [12–20]. The excess O$_{ap}$ atoms are known to be a strong scatterer as well as a Cooper-pair breaker. Therefore the generic properties of the T′-cuprates can be reached only after thorough removal of O$_{ap}$ atoms.

Superconductivity in Ce-free T′-cuprates was first demonstrated in epitaxial thin films of T′-(La,*RE*)$_2$CuO$_4$ grown by molecular beam epitaxy (MBE) [10]. Thin films have an advantage over bulk samples in removal of excess O$_{ap}$ atoms because of a large surface-to-volume ratio and small grain size. Later we also demonstrated parent RE_2CuO$_4$ films (*RE* = Pr, Nd, Sm, Eu, and Gd) by metal organic decomposition to be a superconductor when they are optimally synthesized and annealed [11,21–24]. The contradiction between the published and our results originates from excess O$_{ap}$ atoms. In our work, O$_{ap}$ atoms were cleaned up carefully by a low-temperature reduction process [25], with regular oxygen (O1) atoms in the CuO$_2$ planes mostly preserved.

A question has been raised on the nature of superconductivity in parent T′-RE_2CuO$_4$ [26–28]. Namely the superconductivity is achieved in the truly undoped state or by electron doping via oxygen vacancies at the O2 site in the fluorite RE_2O$_2$ plane. One way to answer this question is to investigate the oxygen nonstoichiometry in T′ cuprates. However, oxygen nonstoichiometry is very difficult to determine in thin films. The most rigorous experiment for this purpose may be neutron diffraction on powder samples to determine the equilibrium site-specific occupancies at the three oxygen sites, regular O1, O2, and interstitial O$_{ap}$. Such experiments require bulk powder samples of T′-RE_2CuO$_4$ with a full superconducting volume fraction. However, it has been difficult to remove excess O$_{ap}$ atoms completely from bulk T′-RE_2CuO$_4$ samples [16,29–32]. Low-temperature reduction heat treatment at 400–500 °C as employed in thin films is not effective because of larger grain size in bulk powder samples than in thin films. On the other hand, high-temperature reduction heat treatment at 900–1000 °C, which is usually employed in Ce doped T′-(*RE*,Ce)$_2$CuO$_4$ bulk samples, decomposes parent T′-RE_2CuO$_4$ since Ce-free compounds are less stable at high temperatures in low p_{O2} than Ce doped compounds [32].

In this article, we report the synthesis of superconducting T′-La$_{2-x}$Sm$_x$CuO$_4$ powder samples via a molten alkaline hydroxide route [25,29]. La^{3+} was chosen because it is empirically known that

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the removal of O_{ap} atoms is easier for larger RE^{3+}. However, T′-La_2CuO_4 is not stable at high temperatures above ~600 °C, which restricts the temperature for reduction heat treatment. Therefore we also prepared Sm doped samples, which are stable at high temperatures. T′-$La_{2-x}Sm_xCuO_4$ should also be undoped because La and Sm ions are both trivalent. The superconductivity is observed in the samples with $x = 0.05$–1.0 and the superconducting volume fraction is nearly 100% at $x = 0.3$–0.7.

2. Experimental

La_2CuO_4 adopts the well-known K_2NiF_4 (abbreviated as T) structure in the synthesis at high temperatures (1000–1200 °C). However, Manthiram and Goodenough [33] suggested that T′-La_2CuO_4 can be synthesized at temperatures below 425 °C. The synthesis temperature below 425 °C is too low to prepare samples by conventional solid-state reaction. Since the diffusion of atoms by thermal energy is limited at low temperatures, it is necessary to employ soft-chemistry synthesis techniques relying on chemical energy instead of thermal energy. We have employed a molten alkaline hydroxide route for the synthesis of $La_{2-x}Sm_xCuO_4$. This method enables the synthesis of cuprates at temperatures as low as 300–400 °C [34–38].

Polycrystalline samples of $La_{2-x}Sm_xCuO_4$ with $x = 0.0$–0.5 were synthesized as follows. First high-purity starting powders of CsOH and Cu_2O were placed in a 25 ml Ag crucible [39] and melted at 400 °C for several hours in flowing N_2 gas. Subsequently high-purity powders of La_2O_3 and Sm_2O_3 were added quickly into the melt of CsOH and Cu_2O, and the crucible was held at 400 °C for another 48–72 h in flowing N_2 gas. The purpose for adding La_2O_3 and Sm_2O_3 powders later is to prevent them from reacting below 400 °C. This procedure is important to obtain the single T′ phase of $La_{2-x}Sm_xCuO_4$ with $x = 0$–0.5 since Cs contamination takes place at reaction temperatures below 400 °C, which results in the formation of the T phase of $(La,Cs)_2CuO_4$. This complicated procedure is not required in the synthesis of $La_{2-x}Sm_xCuO_4$ with $x > 0.5$. In the synthesis of samples with $x = 0.6$–2.0, all the starting powders (CsOH, Cu_2O, La_2O_3, and Sm_2O_3) were placed in a 25 ml Ag crucible and heated at 420–480 °C for 48–72 h in flowing N_2 gas.

In the experiments we used two types of heating apparatuses: a separable flask heated by a mantle heater and a horizontal tube furnace. So far the former was used for the synthesis of samples with $x = 0$–0.5 since it is easier to add La_2O_3 and Sm_2O_3 powders later in a heated Ag crucible. The latter was used for the synthesis of samples with $x = 0.6$–2.0 since the complicated procedure is not required and also the reaction temperatures are higher than the highest temperature (~410 °C) reached by a mantle heater. After the reaction, the melt was decanted and the product was quenched to ambient temperatures. A black polycrystalline powder was isolated by dissolving the flux in water. Reduction for removal of excess O_{ap} atoms was performed for the powders in vacuum of $p < 10^{-4}$ Torr at 600–750 °C for 48–96 h. The synthesis and reduction conditions for each x are summarized in Table 1. The reduction temperature (T_{red}) is slightly below the decomposition temperature for each x. The decomposition of samples can be noticed by Cu metal, one decomposed product of samples [16], deposited on a quartz tube of a furnace used for reduction (not the same as the tube furnace for synthesis above). The T_{red} increases with x except for $x = 0.5$. The crystallinity of the sample of $x = 0.5$ was somewhat lower than that of other x since the synthesis conditions were not optimized because of insufficient reaction temperatures by a mantle heater. It makes T_{red} for $x = 0.5$ lower than T_{red} for neighboring x. The phase identification was performed by X-ray diffraction (XRD). Magnetization measurements were performed using a SQUID magnetometer.

Table 1
Synthesis and reduction conditions for T′-$La_{2-x}Sm_xCuO_4$. The typical grain size of powder samples obtained is also included.

x	Heating apparatus	T_s (°C)	T_{red} (°C)	Grain size (μm)
0.0	Mantle heater	400	600	~10
0.05	Mantle heater	400	650	10–20
0.1	Mantle heater	400	700	10–20
0.2	Mantle heater	400	700	10–20
0.3	Mantle heater	400	700	10–20
0.4	Mantle heater	400	700	10–20
0.5	Mantle heater	400	650	10–20
0.6	Tube furnace	420	700	40–60
0.7	Tube furnace	440	700	40–80
0.8	Tube furnace	440	700	30–50
0.9	Tube furnace	440	700	20–40
1.0	Tube furnace	440	700	40–80
1.3	Tube furnace	440	700	40–80
1.5	Tube furnace	440	700	80–200
2.0	Tube furnace	480	750	20–40

3. Results and discussion

Fig. 1 show the XRD patterns of the polycrystalline powder samples of $La_{2-x}Sm_xCuO_4$. The samples shown in these figures are nearly single-phase T′ with no inclusion of the T phase. The end member, La_2CuO_4, with the single T′ phase can be obtained only in a narrow temperature range between 400 °C and 425 °C. The critical temperature to separate the T′ and T phases of La_2CuO_4 is 425 °C, which is in accord with the prediction by Manthiram and

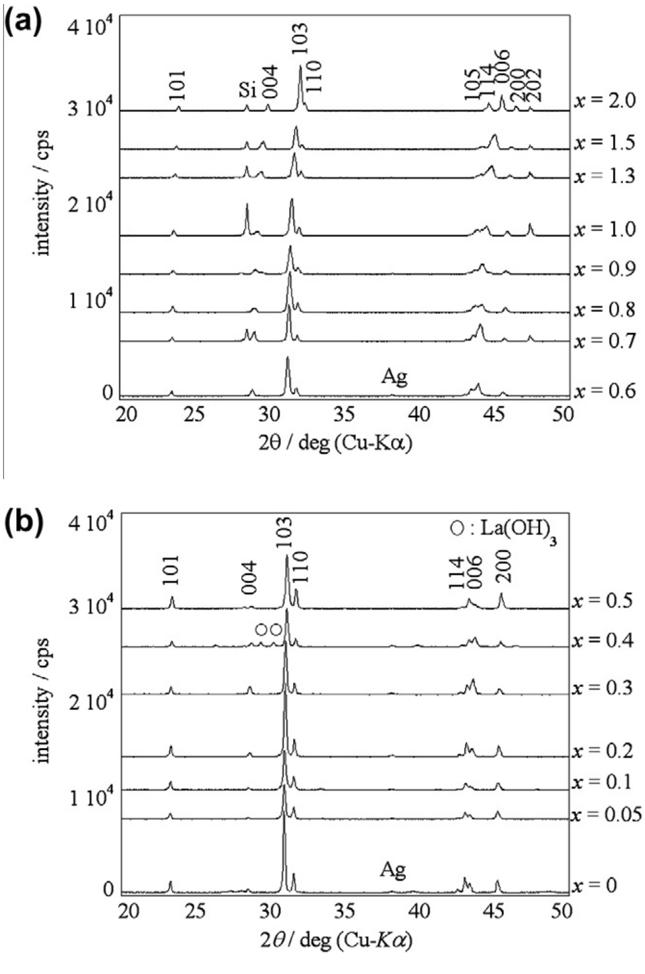

Fig. 1. XRD patterns of T′-$La_{2-x}Sm_xCuO_4$ polycrystalline samples: (a) samples with $x = 0.6$–2.0 prepared by a horizontal tube furnace and (b) samples with $x = 0$–0.5 prepared by a mantle heater.