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# Synthesis and properties of superconducting $T'$-$R_2$CuO$_4$ ($R$=Pr, Nd, Sm, Eu, Gd)

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The parent compounds of high-$T_c$ cuprates have long been considered to be antiferromagnetic insulators. In this Rapid Communication, however, we report that superconductivity is achieved in $T'$-$R_2$CuO$_4$ ($R$=Pr, Nd, Sm, Eu, Gd). Superconducting $T'$-$R_2$CuO$_4$ films were synthesized by using metal-organic decomposition. The highest $T_c$ of $T'$-$R_2$CuO$_4$ is over 30 K, substantially higher than "electron-doped" analogs. Remarkably, Gd$_2$CuO$_4$, even the derivatives of which have not shown superconductivity so far, gets superconducting with $T_c^{\text{onset}}$ as high as ~20 K. The implication of our results is briefly discussed.

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The parent compounds of high-$T_c$ cuprates have long been considered to be antiferromagnetic Mott insulators (charge-transfer insulators). For example, La$_2$CuO$_4$ with the K$_2$NiF$_4$ (abbreviated as $T$) structure is an insulator with no doubt. $R_2$CuO$_4$ ($R$: rare-earth element) with the Nd$_2$CuO$_4$ (abbreviated as $T'$) structure has also been believed to be a Mott insulator since the discovery of "electron-doped" superconductors, $T'$-$(R,\text{Ce})_2$CuO$_4$ in 1989.[1] In this Rapid Communication, however, we report $T'$-$R_2$CuO$_4$ to be superconducting. The origin of the sharp contradiction between the past and our results can be traced to impurity oxygen at the apical site. Empirically, apical oxygen (O$_{\text{ap}}$) atoms in $T'$ cuprates play the role of a very strong scatterer as well as a pair breaker.[2] Therefore the generic phase diagram of the $T'$ cuprates can be reached only after complete removal of O$_{\text{ap}}$ atoms. The report along this line was made initially by Brinkmann *et al.*[3] in 1995. They reported that the superconducting (SC) window for Pr$_{2-x}$Ce$_x$CuO$_4$ expands by their improved reduction process down to $x$=0.04. The expanded SC window can be explained by the suppression of O$_{\text{ap}}$-induced antiferromagnetic order. Employing a thin-film process, we also demonstrated that the superconducting range in $T'$-La$_{2-x}$Ce$_x$CuO$_4$ expands down to $x$=0.045.[4] Furthermore, in the previous paper, we reported superconductivity with $T_c$ ~25 K in $T'$-(La,$R$)$_2$CuO$_4$, which was achieved by state-of-the-art molecular-beam epitaxy (MBE).[5] However, there has been a great controversy on the superconducting nature in $T'$-(La,$R$)$_2$CuO$_4$: band superconductor or electron-doped Mott-Hubbard superconductor due to oxygen deficiencies. One drawback to obtaining a definitive conclusion is that $T'$-(La,$R$)$_2$CuO$_4$ is difficult to synthesize by bulk processes. Therefore they are not amenable to any measurement of oxygen nonstoichiometry, such as chemical analysis or neutron diffraction. Hence only speculative discussions have been made based on transport measurements, such as Hall coefficient and Nernst signal.[6,7] This time, we synthesized superconducting $T'$-$R_2$CuO$_4$ by metal-organic decomposition (MOD), a rather inexpensive and easy-to-implement thin-film process. The key recipe to achieve superconductivity in $T'$-$R_2$CuO$_4$ is low-$P_{\text{O2}}$ firing followed by subsequent low-temperature reduction, which, we believe, cleaned up most of O$_{\text{ap}}$ atoms harmful to high-$T_c$ superconductivity.

Superconducting $T'$-$R_2$CuO$_4$ thin films were prepared by MOD using $R$ and Cu naphthenate solutions. The details of the synthesis are described in Ref. 8. In brief, the stoichiometric mixture of naphthenate solutions was spin coated on substrates, either SrTiO$_3$ (STO) (001) or DyScO$_3$ (DSO) (110).[9] The coated films were first calcined at 400 °C in air to obtain precursors, then fired at 850–900 °C in a tubular furnace under a mixture of O$_2$ and N$_2$, while controlling the oxygen partial pressure ($P_{\text{O2}}$) from $4\times10^{-5}$ atm to 1 atm. Finally the films were "reduced" in vacuum ($<10^{-4}$ Torr $\approx 10^{-7}$ atm) at various temperatures for O$_{\text{ap}}$ removal. The thickness of resultant films was typically 500–1000 Å, although it was not easy to determine it accurately. This is because $T'$-$R_2$CuO$_4$ is fairly acid resistive and it is difficult to make a steep edge for profilometry. The resultant films are single-phase $T'$ and also single-crystalline as achieved via solid-state epitaxy.[8]

The end-member $T'$ cuprates are semiconducting with standard bulk synthesis, as is well known. In contrast, thin films of these compounds are fairly metallic after "reduction."[5] This metallic behavior is probably because thin films are advantageous in O$_{\text{ap}}$ removal due to a large surface-to-volume ratio. However, the optimization of postreduction conditions alone is not sufficient to achieve superconductivity in the parent compounds. The key step for superconductivity is to fire films in a low-$P_{\text{O2}}$ atmosphere; the aim of which is to minimize the amount of impurity oxygen prior to the postreduction process. Figure 1 shows the effect of $P_{\text{O2}}$ during firing, which compares the resistivity ($\rho$) of two Sm$_2$CuO$_4$ films (A and B): film A fired at 900 °C for 1 h in $P_{\text{O2}}$=1 atm, followed by reduction at 750 °C for 10 min, and film B fired at 850 °C for 1 h in $P_{\text{O2}}=2.8\times10^{-3}$ atm, followed by reduction at 440 °C for 10 min. Film A is metallic down to 180 K with $\rho$(300 K) ~ 100 m$\Omega$ cm, but shows resistivity upturn at lower temperatures. By contrast, film B is completely metallic with $\rho$(300 K) ~ 900 $\mu\Omega$ cm and shows superconductivity at $T_c^{\text{onset}}$=28 K ($T_c^{\text{end}}$=25 K). The dramatic effect of low-$P_{\text{O2}}$ synthesis is actually corroborated from the structural aspect. The $c$-axis lattice constant ($c_0$) are 11.97 Å for film A and 11.94 Å for film B. The $c_0$

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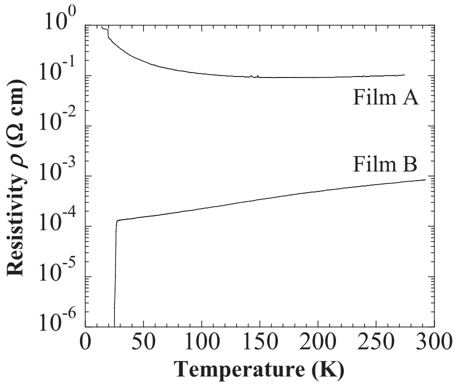

FIG. 1. Temperature dependences of resistivity for $Sm_2CuO_4$ films (A and B) on $SrTiO_3(001)$ substrates. Film A was fired at 900 °C for 1 h in $P_{O2}=1$ atm followed by reduction at 750 °C for 10 min, whereas film B was fired at 850 °C for 1 h in $P_{O2}=2.8\times10^{-3}$ atm followed by reduction at 440 °C for 10 min.

of film A shows a good agreement with the bulk value,[10] whereas the $c_0$ of film B is substantially (~0.03 Å) shorter. Taking account of the well-established trend that the $c_0$ increases with the amount of $O_{ap}$ atoms,[11] our experimental results indicate that low-$P_{O2}$ synthesis is quite effective in preventing $O_{ap}$ atoms from being introduced to lattice.

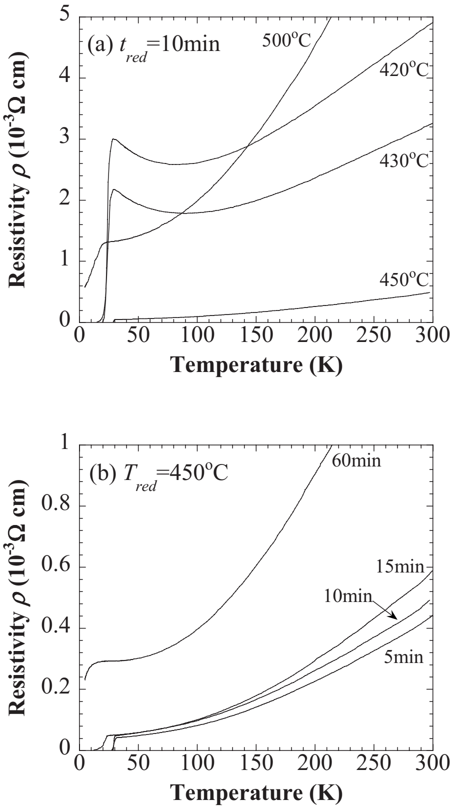

FIG. 2. Reduction dependence of ρ-T for $Pr_2CuO_4$ films on $DyScO_3(110)$ substrates: (a) varying the reduction temperature ($T_{red}$) with the reduction duration ($t_{red}$) fixed at 10 min and (b) varying $t_{red}$ with $T_{red}$ fixed at 450 °C. The films were fired with identical conditions (850 °C for 1 h in $P_{O2}=2.8\times10^{-4}$ atm).

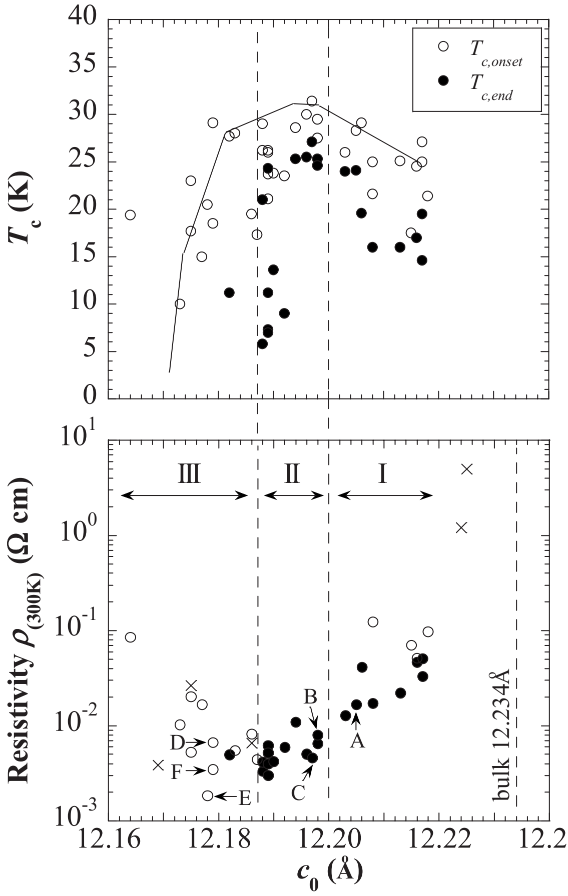

FIG. 3. Plots of $T_c$ and ρ(300 K) versus $c_0$ for all $Pr_2CuO_4$ films on $DyScO_3(110)$ substrates prepared by MOD. Upper ($T_c$ vs $c_0$): open and filled circles stand for $T_c^{onset}$ and $T_c^{end}$. Lower [ρ(300 K) vs $c_0$]: crosses stand for films not showing superconductivity, filled and open circles stand for films showing superconductivity with and without zero resistance, respectively. Data A–F are from the corresponding films in Fig. 4.

Figures 2 show the reduction condition dependence of the film properties for $Pr_2CuO_4$ films. The data were taken from the films fired with identical conditions (850 °C for 1 h in $P_{O2}=2.8\times10^{-4}$ atm) but reduced differently, namely, either with a different reduction temperature ($T_{red}$) for Fig. 2(a) or a different duration ($t_{red}$) for Fig. 2(b). The "as-grown" film (not shown) is semiconducting ($d\rho/dT<0$) and shows no superconductivity. As shown in Fig. 2(a), the reduction with $T_{red}$=420 °C and $t_{red}$=10 min is sufficient for the film to be superconducting ($T_c^{onset}\sim30$ K). Increasing $T_{red}$ up to 450 °C lowers the resistivity and sharpens the superconducting transition. A further increase in $T_{red}$, however, deteriorates the film properties. Similar behavior is observed in Fig. 2(b) by varying $t_{red}$ with $T_{red}$ fixed at 450 °C. A long transition tail appears already with $t_{red}$=15 min and superconductivity disappears with $t_{red}$=60 min although there is almost no trace of decomposition as judged from the XRD pattern. It is most likely that excessive reduction leads to loss of oxygen atoms (O1) in the $CuO_2$ planes, as suggested from the oxygen nonstoichiometry experiments.[12] The reduction with $T_{red}$=450 °C and $t_{red}$=5–10 min provides $Pr_2CuO_4$ films with optimal properties, highest $T_c$ ($T_c^{onset}$ =31.5 K, $T_c^{end}$=27.3 K) and lowest resistivity

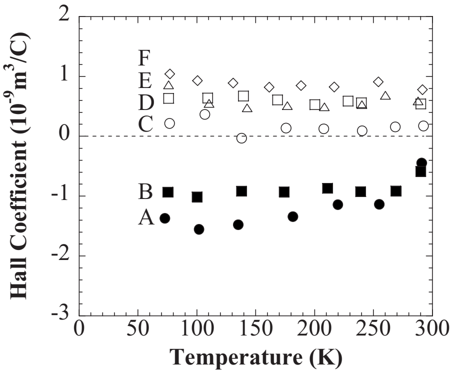

FIG. 4. Reduction dependence of $R_H$ for $Pr_2CuO_4$ films. The films are labeled from A to F according to the reduction strength, which are indicated in Fig. 3. $R_H$ goes up with the change in sign from negative to positive with reduction.

[$\rho(300\ \mathrm{K}) \sim 400\ \mu\Omega$ cm and $\rho(T_c^+) \sim 50\ \mu\Omega$ cm]. The low resistivity value, which is only about twice as high as our best MBE-grown $Pr_{1.85}Ce_{0.15}CuO_4$ films,[13] guarantees the high quality of MOD films.

It is difficult to make a quantitative evaluation of the amount of $O_{ap}$ atoms remaining in thin films, but we have found that one good measure for it may be $c_0$. Figures 3 plot the $\rho(300\ \mathrm{K})$ (lower) and $T_c$ (upper) as a function of $c_0$ for all of our MOD-grown $Pr_2CuO_4$ films. We divide a range of $c_0$ into three regions:

(I) *Insufficient* reduction ($12.23\ \text{Å} \geq c_0 \geq 12.20\ \text{Å}$). The $\rho(300\ \mathrm{K})$ drops rapidly as $c_0$ decreases from the bulk value (broken line). Superconductivity with $T_c^{\mathrm{onset}} \sim 25$ K suddenly appears for $c_0 < 12.22$ Å. Decreasing $c_0$ further toward 12.20 Å, the $T_c^{\mathrm{onset}}$ gradually increases to ~30 K, and the $T_c^{\mathrm{end}}$ also improves.

(II) *Optimal* reduction ($12.20\ \text{Å} \geq c_0 \geq 12.19\ \text{Å}$). The $\rho(300\ \mathrm{K})$ still decreases as $c_0$ decreases, and superconductivity becomes optimum.

(III) *Excessive* reduction ($12.19\ \text{Å} \geq c_0 \geq 12.16\ \text{Å}$). The $T_c^{\mathrm{onset}}$ starts to drop and the superconducting transition becomes broad with $T_c^{\mathrm{end}}$ below 4.2 K, although $\rho(300\ \mathrm{K})$ still decreases until $c_0 \sim 12.18$ Å. With a further decrease in $c_0$ below 12.18 Å, $\rho(300\ \mathrm{K})$ gradually increases and superconductivity eventually disappears.

At first, it should be pointed out that there is no highly insulating state corresponding to a Mott insulator by reduction starting from the as-grown state containing $O_{ap}$. Figures 2 and 3 can be explained by assuming that the two effects, namely, $O_{ap}$ removal and O1 loss, are involved in the reduction process. The predominant effect in region (I) is $O_{ap}$ removal, which improves the film properties. In contrast, the predominant effect in region (III) is O1 loss, which degrades the film properties, although $O_{ap}$ may be removed further as judged from the shrinkage of $c_0$. The $O_{ap}$ removal is slightly quicker than the O1 loss, which results in $O_{ap}$ atoms mostly cleaned up but with O1 atoms mostly preserved, and provides a stage potential for high-$T_c$ superconductivity.

Figure 4 shows the Hall coefficient ($R_H$) of $Pr_2CuO_4$ films. The films are labeled from A to F according to the reduction strength, as correspondingly indicated in Figs. 3. The $R_H$ changes sign with reduction: negative for insufficiently reduced films and positive for excessively reduced films. The optimally reduced film (film C) has nearly $R_H \sim 0$. The data in Fig. 4 qualitatively resembles the reduction dependence of $R_H$ in "optimally doped" $T'$-$Nd_{1.85}Ce_{0.15}CuO_4$ reported by Jiang *et al.*,[14] especially from the fact that $R_H$ goes up and changes sign from negative to positive with reduction. In general, the Hall coefficients in metals are a very complicated function of anisotropic Fermi velocity as well as anisotropic relaxation time, which makes the interpretation nonstraightforward.[15] The simplistic two-band model, although neither quantitative nor realistic, gives some insight for the sign change of $R_H$,

$$R_H = \frac{\mu_p\sigma_p - \mu_n\sigma_n}{(\sigma_p + \sigma_n)^2} = \frac{pe\mu_p^2 - ne\mu_n^2}{(pe\mu_p + ne\mu_n)^2},$$

where $p$ and $n$ are the carrier densities, $\mu_p$ and $\mu_n$ the mobilities, $\sigma_p$ and $\sigma_n$ the conductivities of hole and electron bands. Based on this model, the behavior of $R_H$ in Fig. 4 can be interpreted as follows. We assume that the majority carriers are hole and the minority carriers are electron and also that $O_{ap}$ scatters mainly hole carriers, which is consistent with the recent analytical papers on the transport properties of $Pr_{2-x}Ce_xCuO_4$ films.[16,17] With a fair amount of $O_{ap}$ atoms (insufficiently reduced films), the hole mobility $\mu_p$ is low and $R_H$ is determined by the minority carriers, namely, negative. By cleaning up $O_{ap}$ atoms, the hole mobility $\mu_p$ improves and $R_H$ becomes positive and approaches $\frac{1}{pe}$. The observed $R_H$ of film D to F is $5-10 \times 10^{-10}$ $m^3/C$, which gives $p$ of $1.25-0.625 \times 10^{22}$ holes/$cm^3$, amounting to 1.2–0.6 holes/Cu, namely, almost half filled.

TABLE I. Comparison of $T_c$ between $R_2CuO_4$ and $R_{1.85}Ce_{0.15}CuO_4$. $T_c$'s of $R_{1.85}Ce_{0.15}CuO_4$ are taken from Ref. 18.

| $R$ | $T_c$ of $R_2CuO_4$ (K) | $T_c$ of $R_{1.85}Ce_{0.15}CuO_4$ (K) |
|---|---|---|
| La | | 18.5[a] |
| Pr | 31.5 | 25.0 |
| Nd | 32.5 | 24.0 |
| Sm | 27.5 | 19.0 |
| Eu | 27.5 | 12.0 |
| Gd | 19.0 | 0 |

[a] The highest $T_c$ of $La_{2-x}Ce_xCuO_4$ is 30.5 K at $x=0.08$ (Ref. 4).

Table I is a summary of the $R$ dependence. All $R$'s we have tested show superconductivity except for $R$=La, which does not form the $T'$ structure by MOD.[19] It should be noted that $T_c$ of $T'$-$R_2CuO_4$ is substantially higher than $T_c$ of $T'$-$R_{1.85}Ce_{0.15}CuO_4$. The highest $T_c^{\mathrm{onset}}$ is 32.5 K in $Nd_2CuO_4$. The most remarkable is $Gd_2CuO_4$: there has been no report[20] that $Gd_{2-x}Ce_xCuO_4$ becomes superconducting, whereas $Gd_2CuO_4$ in the present study has $T_c^{\mathrm{onset}}$ as high as 19.0 K.

The key question is the nature of superconductivity in $T'$-$R_2CuO_4$. What one can imagine most easily may be electron-doped Mott-Hubbard superconductivity due to the oxygen (O2) deficiency in the fluorite $R_2O_2$ layers, especially when one sees the resemblance of the reduction dependence in the present paper with the well-known Ce-doping dependence. However, the O2 deficiency in the fluorite $R_2O_2$ planes is unlikely to occur, especially at temperatures as low as 400 °C, since solid-state chemistry tells us that the $R$-O bond is much stronger than the Cu-O bond.[21] In fact, there is no neutron-diffraction experiment[12,22,23] showing any change in the O2 occupancy with reduction, even though some early experiments showed that the O2 occupancy is not full (namely, slightly below 2.00). This indicates that the reduction dependence of physical properties in $T'$-$R_2CuO_4$ cannot be explained by the change in the O2 occupancy. Furthermore the observation of a positive Hall coefficient with reduction may also argue against a simple electron doping mechanism via O2 deficiency. The physics behind the observation of superconductivity in $T'$-$R_2CuO_4$ at present is not yet fully understood. However, the amount of $O_{ap}$ atoms seems to affect the phase diagram severely and even the occurrence of the "Mott-Hubbard"- type insulating state.

In summary, we achieved superconductivity in $T'$-$R_2CuO_4$ ($R$=Pr, Nd, Sm, Eu, Gd), which have been believed as a Mott insulator. The highest $T_c$ of $T'$-$R_2CuO_4$ is over 30 K, substantially higher than electron-doped analogs. Our results alert further experiments to establish the nature of superconductivity, especially the oxygen chemistry in $T'$ cuprates. Since MOD is not fundamentally different from bulk synthesis, superconducting $T'$-$R_2CuO_4$ may be obtainable in bulk form, which enables oxygen nonstoichiometry measurements such as chemical analysis and neutron diffraction.

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