Undoped cuprate superconductors – band superconductors or oxygen-doped Mott-Hubbard superconductors?

M Naito 1,*, O Matsumoto 1, A Utsuki 1, A Tsukada 2, H Yamamoto 3 and T Manabe 4

1 Department of Applied Physics, Tokyo University of Agriculture and Technology, Naka-cho 2-24-16, Koganei, Tokyo 184-8588, Japan
2 Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA
3 NTT Science and Core Technology Laboratory Group, NTT Corporation, 3-1 Morinosato-Wakamiya, Atsugi, Kanagawa 243-0198, Japan
4 National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

E-mail: minaito@cc.tuat.ac.jp

Abstract. Undoped cuprates have long been considered to be antiferromagnetic Mott insulators (charge-transfer insulators). In this article we report that one group of cuprates, namely \( RE_2\text{CuO}_4 \) with the \( \text{Nd}_2\text{CuO}_4 \) (\( T' \)) structure, become superconducting without doping. Our discovery was achieved by metal-organic decomposition, an inexpensive and easy-to-implement thin-film process. The highest \( T_c \) of undoped \( T'-\text{RE}_2\text{CuO}_4 \) is over 30 K, substantially higher than their “electron-doped” analogs. Remarkably, \( \text{Gd}_2\text{CuO}_4 \) even the derivatives of which have not shown superconductivity so far, gets superconducting with \( T_{c \text{ onset}} \) as high as 20 K. Our discovery contradicts with the past results supporting undoped cuprates to be generally insulating. The clue to understanding the sharp contrast between the past and our results is impurity oxygen (\( O_{ap} \)) at the apical site. The implication of our discovery is briefly discussed.

1. Introduction

Undoped cuprates have long been considered to be antiferromagnetic Mott insulators (charge-transfer insulators). For example, \( \text{La}_2\text{CuO}_4 \) with the \( \text{K}_2\text{NiF}_4 \) (abbreviated as \( T \)) structure is an insulator with no doubt. \( \text{RE}_2\text{CuO}_4 \) (\( RE \); rare-earth element) with the \( \text{Nd}_2\text{CuO}_4 \) (abbreviated as \( T' \)) structure has also been believed as a Mott insulator since the discovery of “electron-doped” superconductors, \( T'-\text{(RE,Ce)}_2\text{CuO}_4 \) in 1989 [1]. In this article, however, we report \( T'-\text{RE}_2\text{CuO}_4 \) to be superconducting without doping. The origin of the sharp contradiction between the past and our results can be traced to impurity oxygen (\( O_{ap} \)) at the apical site. Empirically, apical oxygen atoms in \( T' \) cuprates play the role of very strong scatterer as well as pair-breaker, presumably due to magnetic (Kondo) scattering by \( O_{ap} \)-induced Cu spins [2]. Therefore the generic phase diagram of the \( T' \)-cuprates can be reached only after removing apical oxygen atoms completely. The first report along this line was made by Brinkmann et al. in 1995 [3]. They extended the superconducting region of \( \text{Pr}_2\text{Ce}_2\text{CuO}_4 \) (single crystals) down to \( x = 0.04 \) via a novel reduction route. However, their result has not been reproduced successfully by any other group, and its importance has been largely forgotten with time. At almost

* To whom any correspondence should be addressed.
the same time as Brinkmann’s paper appeared, we also observed a clear Fermi edge in undoped Nd$_2$CuO$_4$ films, indicating metallic nature, in in-situ photoemission spectroscopy on MBE-grown films [4]. This observation together with Brinkmann’s result led us to great skepticism on the currently accepted electronic phase diagram for $T’$ cuprates.

In 2003, we discovered superconductivity of $T_c \sim 25$ K in “undoped” $T’$-(La,RE)$_2$CuO$_4$ [5]. This was achieved by the state-of-the-art molecular beam epitaxy (MBE) technique. There has been a great controversy on the superconducting nature of these cuprates: truly undoped or oxygen-deficit electron-doped. One drawback of $T’$-(La,RE)$_2$CuO$_4$ is that they are difficult to synthesize, especially make superconducting, by bulk processes. Therefore they may not be amenable to any measurement on oxygen nonstoichiometry like chemical analysis or neutron diffraction. Hence only speculative discussions have been given on the superconducting nature based on transport measurements like Hall coefficient, Nernst signal, etc. The new undoped superconductors, $T’$-RE$_2$CuO$_4$ (RE = Pr, Nd, Sm, Eu, and Gd), presented in this article, have $T_c$ over 30 K. They were synthesized by metal-organic decomposition (MOD), a rather familiar (lo-tech) thin film process, in contrast to leading-edge (hi-tech) MBE required to produce the first generation of undoped $T’$-(La,RE)$_2$CuO$_4$. Since MOD is not fundamentally different from bulk synthesis, superconducting $T’$-RE$_2$CuO$_4$ may be obtainable in bulk form, which enables oxygen non-stoichiometry measurements such as chemical analysis, neutron diffraction, to reach an unambiguous conclusion over the controversy.

2. Experimental
The superconducting RE$_2$CuO$_4$ thin films were prepared by the MOD method by using RE and Cu naphtenate solutions. The solutions were mixed with the stoichiometric ratio and the mixed solution was spin-coated on substrates. As a substrate, we used SrTiO$_3$ (STO) (100) and DyScO$_3$ (DSO) (110) [6]. The coated films were first calcined at 400°C in air to obtain precursors. Then the precursors were fired at 850 – 900°C in a tube furnace under a mixture of O$_2$ and N$_2$, varying the oxygen partial pressure $P_{O_2}$ from 2 x 10$^{-4}$ atm to 1 atm. Finally the films were “reduced” in vacuum ($< 10^{-4}$ Torr ≈ 10$^{-7}$ atm) at various temperatures for removal of O$_{ap}$. Films with no reduction were also prepared for a reference, and named as “as-grown”. After the reduction, the films were furnace-cooled in vacuum to avoid re-absorption of oxygen. The film thickness was typically 800 Å. The crystal structure and the c-axis lattice constant ($c_0$) of the films were determined with a powder X-ray diffractometer, and the resistivity was measured by a standard four-probe method.

3. Results
Figure 1 shows the X-ray diffraction (XRD) patterns of typical films prepared by MOD. All peaks are sharp and can be indexed to (00$l$) of the Nd$_2$CuO$_4$ structure, indicating that the films are single-phase.

Figure 1. XRD patterns of RE$_2$CuO$_4$ films prepared by MOD. All peaks can be indexed to the (00$l$) reflections of the Nd$_2$CuO$_4$ structure, indicating that the films are single-phase $T’$ and also single-crystalline. The substrate for $RE = Pr$ is DyScO$_3$(110) whereas those for other $RE$ are SrTiO$_3$(001).
and also single-crystalline as achieved via solid-state epitaxy. The (00l) peaks, see, e.g. (008) peaks, shift systematically toward larger 2θ from Pr to Gd, indicating that the c-axis shortens in this order.

Figure 2 shows the superconducting transition of one Nd$_2$CuO$_4$ film. This film has $T_{c\text{onset}}$ of ~ 33 K and $T_{c\text{end}}$ of ~ 30 K, which is the highest record ever reported for $T'$ cuprates. As is well known, the end-member $T'$ cuprates are semiconducting or even insulating with standard bulk synthesis. In contrast, they are fairly metallic in thin film form, especially for large RE$^{3+}$ ions like La, Pr, Nd and Sm. This is, we believe, because thin films may be advantageous due to a large surface-to-volume ratio in removing apical oxygen atoms with regular oxygen atoms intact. However, our many-year attempts to achieve superconductivity by optimizing post-reduction conditions have been unsuccessful except for the MBE-grown $T'$-(La,RE)$_2$CuO$_4$. In this study, however, we adopted a totally different approach from the previous attempts, namely the synthesis of films by MOD in a low-$P_{O_2}$ atmosphere. This aims to minimize the amount of impurity oxygen in advance before the post-reduction process.

Figure 3 shows the effect of $P_{O_2}$ during firing, which compares the resistivity of two Sm$_2$CuO$_4$ films (A and B): film A fired at 900°C for 1 hour in $P_{O_2}$ = 1 atm, followed by reduction at 750°C for 10 min, and film B fired at 850°C for 1 hour in $P_{O_2}$ = 2.8 x $10^{-3}$ atm, followed by reduction at 440°C for 10 min. Film A is metallic down to 180 K with $\rho$(300 K) ~ 100 mΩcm, but shows upturn at lower temperatures. By contrast, film B is all the way metallic with $\rho$(300 K) as low as 900 µΩcm, and shows superconductivity at $T_{c\text{onset}}$ = 28 K ($T_{c\text{end}}$ = 25 K). The dramatic effect of low-$P_{O_2}$ synthesis is actually corroborated from the structural aspect. The c-axis lattice constant of the as-grown film prepared in $P_{O_2}$ = 1 atm is 11.976 Å, in a good agreement with the previously reported bulk value [7], whereas the $c_0$ for the as-grown film prepared in $P_{O_2}$ = 2.8 x $10^{-3}$ atm is 11.922 Å, significantly (~0.05 Å) smaller, indicating that impurity O$_{ap}$ atoms left in the lattice are much fewer. In both the films, the reduction temperature and time were optimized, and we found that there is a substantial difference in the optimal reduction temperature. The films fired in low-$P_{O_2}$ do not stand against reduction at temperatures higher than 500°C, whereas the films fired in $P_{O_2}$ = 1 atm do against reduction temperatures as high as 750°C. Namely the phase stability line appears to shift toward higher temperature or equivalently lower $P_{O_2}$ with increasing the amount of O$_{ap}$ atoms. In both the series, the $c_0$ shortens slightly with reduction time. The superconducting films have $c_0$ of 11.90-11.91 Å.
Figure 4(a) shows the superconducting transitions for different RE. All RE's we have tested show superconductivity except for $RE = La$, which does not form the $T'$ structure by MOD [8]. It should be noted that undoped $T_c$ is substantially higher than electron-doped $T_c$. This is most remarkably demonstrated in Gd$_2$CuO$_4$: there has been no report that electron-doped Gd$_{2-x}$Ce$_x$CuO$_4$ gets superconducting, whereas undoped Gd$_2$CuO$_4$ has $T_c$ onset as high as 20 K. Figure 4(b) shows a summary of the RE-dependence of $T_c$. The $T_c$ of electron-doped $T'$ shows a steep dependence on RE, whereas the $T_c$ onset of undoped $T'$ is rather flat, and about 30 K except for Gd. Lower $T_c$ in $RE = Gd$ may not be intrinsic but most likely due to the material problem that O$_1$ removal is difficult for smaller $RE^{3+}$. We are aware that currently obtained $T_c$ of undoped $T'$ is substantially process-dependent, and are not yet sure how much Kelvin the intrinsic $T_c$ reaches.

4. Discussion

The key issue is the nature of superconductivity in the nominally undoped $T'$-RE$_2$CuO$_4$. Are these materials (a) hole-doped or (b) electron-doped or (c) truly undoped? At first, it is safe to exclude hole-doped superconductivity because it is well-known that excess oxygen makes $T'$ parent compounds more insulating, which is in contrast to the $T$-La$_2$CuO$_4$ case [9]. Electron doping due to oxygen deficiencies has been most frequently raised as a possibility to our previous discovery of the first generation undoped superconductors, $T'$-La$_{2-x}$RE$_x$CuO$_4$. Recently, the groups of University of Maryland in US [10] and Hefei National Laboratory in China [11] claimed, based on their results of transport measurements (resistivity, Hall effect, Nernst effect), that nominally undoped $T'$-La$_{2-x}$RE$_x$CuO$_4$ may be, in reality, electron-doped due to oxygen deficiencies in the fluorite layers or in the CuO$_2$ layers. But it has to be kept in mind that these transport parameters are dependent on not only the subtle features ($d\sigma(k)/dk$) of energy bands but also the anisotropic relaxation time at Fermi surface in metals, which makes the interpretation not straightforward in contrast to semiconductors, as one can see in the conventional solid-state physics textbooks [12, 13]. Hence one cannot address the origin of the carriers unambiguously only from transport measurements. From a solid-state chemistry point of view, the oxygen (O1) deficiency in the CuO$_2$ planes may occur. But the substantial loss of O1 kills the superconductivity and eventually makes films insulating and even transparent with the $T'$ structure preserved, which was demonstrated by the detailed work on the effect of oxygen non-stoichiometry to superconductivity performed more than a decade ago by Maryland group [14] and has also been confirmed by our recent work [15].

Figure 4. (a) Resistivity of $T'$-RE$_2$CuO$_4$ ($RE = Pr, Nd, Sm, Eu$ and Gd) films and (b) $RE$ dependence of $T_c$ ($T_c$ onset: $\circ$, $T_c$ end: $\bullet$).
Fig. 5. Decomposition lines of K$_2$NiF$_4$-type or Nd$_2$CuO$_4$-type transition-metal oxides in a comparison with simple transition-metal oxides in a $P_{O_2}$-$1/T$ plane after [17]. It should be noted that $T$-La$_2$CuO$_4$, $T$-Pr$_2$CuO$_4$, $T$-Nd$_2$CuO$_4$ as well as $T$-La$_2$NiO$_4$, $T$-La$_2$CoO$_4$ decompose just beneath the decomposition line of each simple oxide (CuO, NiO, CoO), indicating that the decomposition of these complex oxides is triggered by break of Cu-O or Ni-O, or Co-O bonds but with La-O or RE-O bonds intact. It should be noticed that the decomposition lines for NiO-Ni and CoO-Co almost coincide.

The oxygen (O$_2$) deficiency in the fluorite $RE_2$O$_2$ planes is unlikely to occur since solid-state chemistry tells us that the $RE$-O bond is much stronger than the Cu-O bond. $T$-La$_2$CuO$_4$ and $T$-$RE_2$CuO$_4$ can be regarded as a stack of strongly bonded La$_2$O$_2$ or $RE_2$O$_2$ layers and weakly bonded CuO$_2$ layers. The former layers partially help in protecting the oxygen loss from the latter layers, as can be guessed from the phase stability lines of these compounds (see Fig. 5). Therefore, loss of oxygen takes place first at CuO$_2$ layers that should degrade superconductivity as mentioned above. The nature of chemical bonds in cuprates can be learned in the paper by Michel and Raveau [16] written in 1984 before the discovery of high-$T_c$ superconductivity. It is also supported by Fig. 5, which illustrates the decomposition line of K$_2$NiF$_4$-type or Nd$_2$CuO$_4$-type transition-metal oxides in $P_{O_2}$-$1/T$ plane [17]. $T$-La$_2$CuO$_4$, $T$-Pr$_2$CuO$_4$, $T$-Nd$_2$CuO$_4$ as well as $T$-La$_2$NiO$_4$, $T$-La$_2$CoO$_4$ decompose just beneath the decomposition line of each simple oxide (CuO, NiO, CoO), but well above the La$_2$O$_3$ decomposition line. It indicates that the decomposition of these complex oxides is triggered by break of Cu-O or Ni-O, or Co-O bonds but with La-O or $RE$-O bonds intact. Hence, at present, we are thinking that the most likely is undoped superconductivity. This should be confirmed in future by unambiguous experiments such as thermogravimetry, iodometry titration, and neutron diffraction, on well-qualified oxygen-homogeneous samples. Since MOD is not fundamentally different from bulk synthesis, superconducting $T$-$RE_2$CuO$_4$ may be obtainable in bulk form, which enables such measurements. Furthermore the answer for undoped or doped can be gained from the probes to the electronic state such as X-ray absorption spectroscopy, photoemission spectroscopy.

Our scenario explaining superconductivity in undoped cuprates is that, with the charge transfer gap collapsed as suggested from the Madelung potential calculation [18], the bottom of the Cu 3$d$ upper Hubbard band merges into the top of the O 2$p$ band in $T$-cuprates or that $T$-cuprates are simply band superconductors. The latter scenario argues sharply against the currently accepted “doped Mott-insulator scenario” for high-$T_c$ superconductivity. The “band-superconductor scenario” was ruled out
at the initial stage of high-$T_c$ research because the end member, $T$-La$_2$CuO$_4$, is an insulator. But we strongly suggest that this possibility has to be re-examined since we have now demonstrated that the insulating behaviour of the end-member cuprates is not universal.

5. Summary
We discovered superconductivity in $T'$-RE$_2$CuO$_4$ ($RE = Pr, Nd, Sm, Eu,$ and Gd) that have been believed as a Mott insulator. The synthesis is rather simple and inexpensive, namely low-$P_{O_2}$ firing and subsequent low-temperature reduction. One point to be emphasized is that low-$P_{O_2}$ phase field has been almost unexplored in the search for new superconductors because of the belief that high-$P_{O_2}$ were necessary in the synthesis of Cu$^{2+}$ compounds. The highest $T_c$ of undoped $T'$-RE$_2$CuO$_4$ is over 30 K, substantially higher than those of “electron-doped” analogs. It is the most likely that these superconductors are truly undoped although it has to be established in future works.

Acknowledgments
The authors thank Dr. Y. Krockenberger and Dr. J. Shimoyama for stimulating discussions, and Dr. T. Kumagai for support and encouragement. The work was supported by KAKENHI B (18340098) from Japan Society for the Promotion of Science (JSPS).

References
[1] Tokura Y, Takagi H and Uchida S 1989 Nature 337 p345.
[2] Sekitani T, Naito M and Miura N 2003 Physical Review B 67 p174503.
[3] Brinkmann M, Rex T, Bach H and Westerholt K 1995 Physical Review Letters 74 p4927.
[4] Yamamoto H, Naito M and Sato H 1997 Physical Review B 56 p2852.
[5] Tsukada A, Krockenberger Y, Noda M, Yamamoto H, Manske D, Alff L and Naito M 2005 Solid State communications 133 p427.
[6] DyScO$_3$ has the GdFeO$_3$, distorted perovskite, structure. The (110) face of GdFeO$_3$ structure is equivalent to the (100) face of pseudo-perovskite structure. DyScO$_3$ single-crystal substrates are available through Crystec GmbH, Germany.
[7] Uzumaki T, Hashimoto K and Kamehara N 1992 Physica C 202 p175.
[8] $T'$-La$_2$CuO$_4$ can be synthesized by bulk synthesis with a very special recipe (Chou et al. 1990 Physical Review B 42 p6172) or by molecular beam epitaxy [9].
[9] Tsukada A, Greibe T and Naito M 2002 Physical Review B 66 p184515.
[10] Yu W, Liang B, Li P, Fujino S, Murakami T, Takeuchi I and Greene R L 2007 Physical Review B 75 p020503.
[11] Zhao L, Wu G, Liu R H and Chen X H 2007 Applied Physics Letters 90 p072503.
[12] Kittel C 1963 Quantum Theory of Solids.
[13] Ziman J M 1960 Electrons and Phonons.
[14] Jiang Wu, Mao S N, Xi X X, Jiang Xiuguang, Peng J L, Venkatesan T, Lobb C J and Greene R L 1994 Physical Review Letters 73 p1291.
[15] Tsukada A, Noda M, Yamamoto H and Naito M 2005 Physica C 426-431 p459.
[16] Michle C and Raveau B 1984 Revue de Chimie Minerale 21 p407.
[17] Petrov A N, Cherepanov V A, Zuyev A Yu and Zhukovcky V M 1988 Journal of Solid State Chemistry 77 p1.
[18] Tsukada A, Shibata H, Noda M, Yamamoto H and Naito M 2006 Physica C 445-448 p94.