Reduction dependence of superconductivity in undoped T’ cuprates

Osamu Matsumotoa, Aya Utsuki, Akio Tsukada, Hideki Yamamoto, Takaaki Manabe, *Michio Naito

a Department of Applied Physics, Tokyo University of Agriculture and Technology
Naka-cho 2-24-16, Koganei, Tokyo 184-8588, Japan

b Geballe Laboratory for Advanced Materials, Stanford University,
Stanford, California 94305, USA

c NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya,
Atsugi, Kanagawa 243-0198, Japan

d National Institute of Advanced Industrial Science and Technology (AIST)
Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

*) Corresponding author. Address: Department of Applied Physics, Tokyo University of Agriculture and Technology, Naka-cho 2-24-16, Koganei, Tokyo 184-8588, Japan.
Tel. +81 42 388 7229; fax: +81 42 385 6255. E-mail address: minaito@cc.tuat.ac.jp.
Reduction dependence of superconductivity in undoped T’ cuprates

Osamu Matsumotoa, Aya Utsuki, Akio Tsukadab, Hideki Yamamotoc, Takaaki Manabed, and *Michio Naitoa

a Department of Applied Physics, Tokyo University of Agriculture and Technology
Naka-cho 2-24-16, Koganei, Tokyo 184-8588, Japan

b Geballe Laboratory for Advanced Materials, Stanford University,
Stanford, California 94305, USA

c NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato-Wakamiya,
Atsugi, Kanagawa 243-0198, Japan

d National Institute of Advanced Industrial Science and Technology (AIST)
Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan
Abstract

We have recently achieved superconductivity in undoped T’-RE$_2$CuO$_4$ ($RE$: Pr, Nd, Sm, Eu, and Gd), using epitaxial thin films by metal organic decomposition. The key recipes to achieve superconductivity are low-$P_{O_2}$ firing and subsequent vacuum reduction to minimize the amount of impurity oxygen atoms, which are very harmful to high-$T_c$ superconductivity. In this article, we report our investigation on the reduction dependence of superconductivity of T’-RE$_2$CuO$_4$. For thin films, the amount of remnant O$_{ap}$ atoms is difficult to evaluate but we propose that one good measure for this may be the $c$-axis lattice constant, which tells us whether the reduction is insufficient or excessive.

PACS: 74.10.+v, 74.25.Dw, 74.62.Bf, 74.72.Dn, 74.78.Bz

Key words: High-$T_c$ superconductivity, Mother compounds, Undoped superconductors, Nd$_2$CuO$_4$ structure, Apical oxygen

*) Corresponding author. Address: Department of Applied Physics, Tokyo University of Agriculture and Technology, Naka-cho 2-24-16, Koganei, Tokyo 184-8588, Japan. Tel. +81 42 388 7229; fax: +81 42 385 6255. E-mail address: minaito@cc.tuat.ac.jp.
Introduction

Very recently we have reported superconductivity in undoped T'-RE$_2$CuO$_4$ ($RE$: Pr, Nd, Sm, Eu, and Gd) [1,2]. The $T_c$ reaches ~ 33K in Nd$_2$CuO$_4$, which is the highest ever reported for T’ cuprates. The specimens have been prepared in thin-film forms by metal organic decomposition (MOD). In order to achieve superconductivity in undoped T'-RE$_2$CuO$_4$, low-$P_{O2}$ firing and subsequent low-temperature vacuum reduction are prerequisite. This process minimizes the amount of impurity apical oxygen (O$_{ap}$) atoms left in the lattice, which are very harmful to high-$T_c$ superconductivity. However, it turned out that prolonged reduction degrades the film properties, and eventually makes films transparent and insulating with the T’ structure preserved [1,3], implying that removal of O$_{ap}$ proceeds with loss of oxygen (O1) indispensable for superconductivity in the CuO$_2$ planes. Hence the process window (phase field) to obtain superconducting films is rather narrow, especially in the case of Eu$_2$CuO$_4$ and Gd$_2$CuO$_4$.

The most scientific way to optimize the O$_{ap}$ removal process with O1 intact is to rely on the data of the site-specific occupancy for O$_{ap}$, O1 and also O2 in the fluorite $RE_2$O$_2$ layers, as a function of temperature and oxygen partial pressure. Such data, in principle, are obtainable by neutron diffraction experiments [4,5], but comprehensive data are unavailable at present. Furthermore not only thermodynamics but also kinetics, namely oxygen diffusion, have to be taken into account in the low-temperature processes; the size and shape of specimens (e.g., bulk vs film) will significantly affect the process parameters. In this article, we propose an alternative method to optimize superconductivity in undoped T'-RE$_2$CuO$_4$. Our method relies on the empirical trend that the c-axis lattice constant ($c_0$) increases with the amount of O$_{ap}$ atoms. For each
RE, we plotted the $T_c$ and resistivity of all films prepared with different firing and reduction recipes as a function of $c_0$, then we found behavior universal to all RE, namely a crossover from an insufficiently to excessively reduced state. Based on this trend, we derived the optimal $c_0$ value for superconductivity.

**Experimental**

The superconducting $RE_2CuO_4$ thin films were prepared by MOD using RE and Cu naphthenate solutions. The details of our MOD method are described elsewhere [1]. Briefly, the stoichiometric mixture of naphthenate solutions was spin-coated on SrTiO$_3$ (STO) (100) or DyScO$_3$ (DSO) (110) substrate [6]. The coated films were first calcined at 400°C in air to obtain precursors, then fired at 850°C – 875°C in a tubular furnace under a mixture of O$_2$ and N$_2$, controlling the oxygen partial pressure $P_{O_2}$ from $4 \times 10^{-5}$ atm to $2 \times 10^{-3}$ atm. Finally the films were reduced in vacuum ($< 10^{-4}$ Torr ≈ $10^{-7}$ atm) at various temperatures ($T_{\text{red}} = 420 \sim 600^\circ C$) and time ($t_{\text{red}} = 5 \sim 60$ min) for $O_{\text{ap}}$ removal. The film thickness was typically 800 Å. The lattice constant was determined from the peak positions in $\theta$-2$\theta$ scans in X-ray diffraction.

**Results & Discussion**

Figures 1 show the $\rho(300 \text{ K})$ and $T_c$ as a function of $c_0$ for all Pr$_2$CuO$_4$ films prepared on DSO substrates with different $T_{\text{red}}$ and $t_{\text{red}}$. The $\rho(300\text{K})$ decreases rapidly as the $c_0$ decreases from the bulk value (broken line) [7], and has a minimum around $c_0 \sim 12.18$ Å. A further decrease of $c_0$ leads to a gradual increase of $\rho(300\text{K})$. We can divide a range of $c_0$ into the following three regions.
Region I: *insufficient* reduction (12.23 Å ≥ \(c_0\) ≥ 12.20 Å)

The \(\rho(300\text{K})\) decreases rapidly with decreasing \(c_0\). Superconductivity with \(T_{c\text{onset}} \sim 25\) K suddenly appears for \(c_0 < 12.22\) Å. Decreasing \(c_0\) towards 12.20 Å, the \(T_{c\text{onset}}\) gradually increases to ~ 30 K, and the \(T_{c\text{end}}\) also improves.

Region II: *optimum* reduction (12.20 Å ≥ \(c_0\) ≥ 12.19 Å)

The \(\rho(300\text{K})\) decreases gradually with decreasing \(c_0\), and optimum superconductivity is obtained at \(c_0 \sim 12.195\) Å with \(T_{c\text{onset}} > 30\) K and \(T_{c\text{end}} > 27\) K.

Region III: *excessive* reduction (12.19 Å ≥ \(c_0\) ≥ 12.16 Å)

The \(\rho(300\text{K})\) still decreases with decreasing \(c_0\) until 12.18 Å, but the \(T_{c\text{onset}}\) starts to decrease and the superconducting transition becomes broad with \(T_{c\text{end}}\) below 4.2 K. With a further decrease of \(c_0\) below 12.18 Å, the resistivity gradually increases and superconductivity eventually disappears.

Figure 2 shows the typical temperature dependences of resistivity, \(\rho(T)\), in the three regions. The \(\rho(T)\) of film A in region I shows an upturn at low temperatures, which is a feature specific to *insufficient* reduction. Film B in region II shows the best superconductivity. Further reduced film C in region II is even more metallic but with reduced \(T_c\). Film D in region III shows only a trace of superconductivity but is still metallic in the whole temperature range with no low-temperature upturn, a feature that distinguishes *excessive* reduction from *insufficient* reduction.

The behavior observed in Figs. 1 and 2 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 removal of O\textsubscript{ap}, which improves the film properties. In contrast, the predominant in region III is loss of O\textsubscript{1}, which degrades the film properties, although O\textsubscript{ap} may be removed further in region III as judged from the further shrinkage of $c_0$ [8]. This interpretation means that the removal of O\textsubscript{ap} is slightly quicker than the loss of O\textsubscript{1}, which realizes the situation with O\textsubscript{ap} atoms mostly cleaned up but with O\textsubscript{1} atoms mostly preserved, and provides a stage potential for high-$T_c$ superconductivity as in region II.

Nd\textsubscript{2}CuO\textsubscript{4} and Eu\textsubscript{2}CuO\textsubscript{4} show behavior similar to Pr\textsubscript{2}CuO\textsubscript{4} as seen in Figs. 3. The $c_0$ value optimal to superconductivity for all RE is summarized in Table I. The region showing a full superconducting transition (filled circles) is narrower in Eu\textsubscript{2}CuO\textsubscript{4} as compared with Pr\textsubscript{2}CuO\textsubscript{4} or Nd\textsubscript{2}CuO\textsubscript{4}. The window is the narrowest in Gd\textsubscript{2}CuO\textsubscript{4}, in which the superconducting samples were obtained but with poor reproducibility even by nominally identical sample preparation. One can explain this RE dependence from a solid-state-chemistry point of view. As explained above, the two requirements, (1) to preserve O\textsubscript{1} and (2) to clean up O\textsubscript{ap}, have to be satisfied for superconductivity to appear. The RE dependent solid-state chemistry tells us that the O\textsubscript{1} binding energy is higher and the O\textsubscript{ap} binding energy lower for a larger RE ion. The former trend can be derived from the RE dependence of the enthalpy of formation for T’-RE\textsubscript{2}CuO\textsubscript{4} (-329.0 kJ/mol for Pr, -298.3 kJ/mol for Nd, -300.1 kJ/mol for Sm, -240.6 kJ/mol for Eu, and -234.4 kJ/mol for Gd) [9-12]. The latter trend is deducible from the thermogravimetric analysis (TG) by Zhu and Manthiram on the O\textsubscript{ap} desorption process for T’-RE\textsubscript{2}CuO\textsubscript{4} [13-15], which demonstrated that the desorption temperature of O\textsubscript{ap} is lower for a larger RE ion. Both indicate that the requirements for superconductivity are more difficult to satisfy for a smaller RE ion.
We have also attempted to remove O\textsubscript{ap} for Gd\textsubscript{2}CuO\textsubscript{4} films by a reduction process close to thermal equilibrium, namely by lowering $T_{\text{red}}$ and increasing $t_{\text{red}}$ to see any improvement in reproducibility, but the results turned out to be worse. Figures 4 show the XRD patterns of Gd\textsubscript{2}CuO\textsubscript{4} films reduced in vacuum at 260°C – 300°C for 13 hours. For comparison, the XRD pattern of an optimally reduced film ($T_{\text{red}} = 440$ °C, $t_{\text{red}} = 10$ min, $T_{\text{c onset}} \approx 19$ K) is also included in Figs. 4. As $T_{\text{red}}$ is increased from 230°C to 300°C, the (0010) peak shows no smooth shift, but a jump from 81.0° (as-grown) to 81.9° at around $T_{\text{red}} \sim 270$ °C ($2\theta$ = 81° and 81.9°, corresponding to $c_0 = 11.864$ Å and 11.759 Å, respectively). A peak split is discernible at 256°C and 280°C, indicating the coexistence of insufficiently and excessively reduced portions with no optimally reduced portion in the films. The film with $T_{\text{red}} = 230$°C was semiconducting whereas the film with $T_{\text{red}} = 300$°C was transparent and insulating (extremely excessive reduction). In contrast, the superconducting Gd\textsubscript{2}CuO\textsubscript{4} film shows a single peak, although somewhat broad, at $c_0 = 11.805$Å. This result indicates that it is difficult to clean up O\textsubscript{ap} atoms with O\textsubscript{1} intact by the reduction process close to thermal equilibrium following thermodynamics, especially for smaller $RE$. The binding energies of interstitial O\textsubscript{ap} and regular O\textsubscript{1} seem to be very close in T’-RE\textsubscript{2}CuO\textsubscript{4}.

**Summary**

We proposed that the $c$-axis lattice constant, $c_0$, is a quite useful parameter to optimize the reduction process to achieve superconductivity in undoped T’-RE\textsubscript{2}CuO\textsubscript{4} since $c_0$ reflects the amount of remnant O\textsubscript{ap}. The plots of $T_c$ and resistivity as a function of $c_0$ demonstrate a crossover from insufficiently to excessively reduced states, and tell us whether the reduction is insufficient (O\textsubscript{ap} still remains) or excessive (O\textsubscript{1} goes
out). Based on this trend, we obtained the $c_0$ value optimal for superconductivity. We also point out that the reduction process close to thermal equilibrium is not good for removing $O_{ap}$, but that the kinetics in reduction is quite important for optimizing superconductivity.

**Acknowledgements**

The authors thank Dr. Y. Krockenberger and Dr. J. Shimoyama for stimulating discussions, and Dr. T. Kumagai for support and encouragement. They also thank Crystec GmbH, Germany for developing new $RESeO_3$ substrates. The work was supported by KAKENHI B (18340098) from Japan Society for the Promotion of Science (JSPS).
References

[1] O. Matsumoto, A. Utsuki, A. Tsukada, H. Yamamoto, T. Manabe, and M. Naito, Physica C 468 (2008) 1148.

[2] M. Naito, O. Matsumoto, A. Utsuki, A. Tsukada, H. Yamamoto, and T. Manabe, J. Phys. Conf. Ser. 108 (2008) 012037.

[3] S. N. Mao, W. Jiang, X. X. Xi, Q. Li, J. L. Peng, R. L. Greene, T. Venkatesan, D. P. Beesabathina, L. Salamanca-Riba, and X. D. Wu, Appl. Phys. Lett. 66 (1995) 2137.

[4] P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, J. L. Peng, and R. L. Greene, Phys. Rev. B 49 (1994) 15322.

[5] A. J. Schultz, J. D. Jorgensen, J. L. Peng, and R. L. Greene, Phys. Rev. B 53 (1996) 5157.

[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] T. Uzumaki, K. Hashimoto, and N. Kamehara, Physica C 202 (1992) 175.

[8] There is no report indicating that O1 loss leads to the shrinkage of $c_0$.

[9] Yu. D. Tretyakov, A. R. Kaul, and N. V. Makukhin, J. Solid State Chem. 17 (1976) 183.

[10] A. N. Petrov, V. A. Cherepanov, A. Yu. Zuyev, and V. M. Zhukovsky, J. Solid State Chem. 77 (1988) 1.

[11] A. N. Petrov, A. Yu. Zuyev, and V. A. Cherepanov, Russian J. Phys. Chemistry 62 (1988) 1613.
[12] Y. Idemoto, I. Oyagi, and K. Fueki, Physica C 195 (1995) 269.
[13] Y. T. Zhu and A. Manthiram, Physica C 224 (1994) 256.
[14] Y. T. Zhu and A. Manthiram, Phys. Rev. B 49 (1994) 6293.
[15] Y. T. Zhu and A. Manthiram, J. Solid State Chem. 114 (1995) 491.
Table I. c-axis lattice constants of T'-$RE_2CuO_4$ for bulk and superconducting film samples. The bulk $c_0$ is taken from ref. 7.

| $RE$ | $c_0$ (bulk) [Å] | $c_0$ (optimum film) [Å] |
|------|----------------|--------------------------|
| Pr   | 12.234         | 12.197                   |
| Nd   | 12.163         | 12.121                   |
| Sm   | 11.972         | 11.938                   |
| Eu   | 11.903         | 11.855                   |
| Gd   | 11.881         | 11.805                   |
Figure captions

Figures 1 Plots of $T_c$ (upper) and $\rho(300 \text{ K})$ (lower) versus $c_0$ for all Pr$_2$CuO$_4$ films on DSO substrates prepared by MOD. Upper: open and filled circles represent $T_c^{\text{onset}}$ and $T_c^{\text{end}}$. Lower: filled circles, open circles and crosses represent films showing superconductivity with zero resistance, ones showing superconductivity without zero resistance, and ones showing no trace of superconductivity, respectively. The dotted lines are guides for eye. We divide a range of $c_0$ into the following three regions: insufficient (region I), optimum (region II), and excessive (region III) reduction. The typical $\rho(T)$ data in the three regions (films A – D) are shown in Fig. 2.

Figure 2 Typical temperature dependences of resistivity of Pr$_2$CuO$_4$ films with insufficient, optimum, and excessive reduction. Data A-D are from the corresponding films in Figs. 1.

Figures 3 Plots of $\rho(300 \text{ K})$ versus $c_0$ for Nd$_2$CuO$_4$ films (upper) and Eu$_2$CuO$_4$ films (lower) prepared by MOD. The meanings of symbols are the same as in Figs. 1. The dotted lines are guides for eye.

Figures 4 XRD patterns of Gd$_2$CuO$_4$ films on STO reduced at $T_{\text{red}} = 260^\circ\text{C} – 300^\circ\text{C}$ for $t_{\text{red}} = 13\text{h}$ and optimally reduced film ($T_{\text{red}} = 440^\circ\text{C}$, $t_{\text{red}} = 10\text{ min}$, $T_c^{\text{onset}} \sim 19\text{ K}$). The patterns near the (0010) peak of T’ are enlarged in the lower panel.
Figure 1

![Graph showing transition temperatures and resistivity against c₀ (Å). The graph is divided into three sections: I, II, and III. The labels for the axes are:
- Vertical axis: \( T_c (K) \)
- Horizontal axis: \( c_0 (Å) \)
- For resistivity, the axis is on a logarithmic scale, with labels from \( 10^{-1} \) to \( 10^3 \) (mΩcm). The graph includes markers and dashed lines to indicate different regions and trends.]

- There are markers labeled as \( T_{onset} \) and \( T_{end} \).
Figure 2

Resistivity $\rho$ (m$\Omega$cm) vs. Temperature (K)

- A
- B
- C
- D

$x^{1/5}$
Figure 3

The figure shows the resistivity $\rho_{(300 \text{ K})}$ (in m$\Omega$cm) as a function of $c_0$ (Å) for two different bulk values, 12.163 Å and 11.903 Å, indicated by the dashed lines. The data points are plotted on a logarithmic scale, with symbols indicating different experimental conditions or measurements.
Figure 4

![Graph showing the variation of intensity with 2θ for different temperatures and the optimum temperature of 440°C/10min.](image-url)