Dependence of $T_c$ on the $RE$-ion size in (RE, Ca)Ba$_2$Cu$_3$O$_6$

K Nakagawa, Y Sumino, H Chiba, K Kim, T Noji, M Kato and Y Koike

Department of Applied Physics, Graduate School of Engineering, Tohoku University, 6-6-05 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

E-mail: nakagawak@teion.apph.tohoku.ac.jp

Abstract. Polycrystalline samples of $RE_{x}Ca_{3-x}Ba_{2}Sr_{2}Cu_{3}O_{6}$ ($RE$ = rare-earth elements) without oxygen in the Cu(1)O chain have been prepared by the conventional solid-state reaction method. No superconductivity appears for larger $RE =$ Nd, Gd, Dy, Y, Yb, Lu, while superconductivity with $T_c$ ~ 50 K appears for smaller $RE = Y$, Yb, Lu. This is presumably because holes produced by the Ca-substitution for $RE$ are more supplied to the conductive Cu(2)O$_2$ plane than to Cu(1) as the lattice becomes small. The maximum $T_c$ = 53 K for $RE = Lu$ is considerably lower than 90 K for $REBa_2Cu_3O_7$. This may be due to the low hole-concentration in the Cu(2)O$_2$ plane.

1. Introduction

Among numerous high-$T_c$ superconducting cuprates, the so-called $RE$-123 system of $REBa_2Cu_3O_7$ ($RE$ = rare-earth elements) is the most promising superconductor for practical application because of its high critical-current-density. However, its $T_c$ ~ 90 K is too low for practical application at the liquid nitrogen temperature. Therefore, the development of superconductors with $T_c$ ~ 100 K in the $RE$-123 system is desired.

It is known that $T_c$ increases with an increase of the distance between Cu in the CuO$_2$ plane and the so-called apical-oxygen $O_a$. The distance between Cu(2) in the CuO$_2$ plane and $O_a$ distance in $REBa_2Cu_3O_6$ ($RE$ : rare-earth elements) is longer than that in $REBa_2Cu_3O_7$ with $T_c$ ~ 90 K [1], so that its $T_c$ is expected to increase up to more than 90 K. However, $REBa_2Cu_3O_6$ without the oxygen $O_{chain}$ in the Cu(1)O chain is an insulator, because $O_{chain}$ ions supply holes to the Cu(2)O$_2$ plane.

There have been several reports on the appearance of superconductivity by doping holes through the substitution of Ca$^{2+}$ for $RE^{3+}$ in $REBa_2Cu_3O_6$. In the case of $RE = Y$, the solubility limit of Ca is only $x = 0.2$ in $RE_1-xCa_{x}Ba_{2}Cu_3O_6$ and the doped holes are not sufficient. For this reason, the value of $T_c$ is much lower than 90 K in YBa$_2$Cu$_3$O$_7$ and varies from 10-50 K depending on the reports, which may be due to the difference in the oxygen content or the definition of $T_c$ [2-5]. On the other hand, no superconductivity appears for $RE =$ Er, Gd and Eu in $RE_{0.8}Ca_{0.2}Ba_{2}Cu_3O_6$ [4]. As for small $RE =$ Yb, moreover, Fujinami et al. [6] have reported superconductivity in Yb$_{1-y}Ca_yBa_{1.6}Sr_{0.4}Cu_{2}O_{6+8}$ in which the solubility limit of Ca is extended up to $x(Ca) = 0.40$ through the partial substitution of Sr for Ba such that holes are doped sufficiently. In this system, superconductivity appears for $x(Ca) \geq 0.2$ and $T_c$ increases up to about 50 K as $x(Ca)$ increases. Unfortunately, it does not reach 90 K.

In this paper, we report the dependence of $T_c$ on $RE$ ionic size in $RE_{1-x}Ca_{x}Ba_{1.6}Sr_{0.4}Cu_{2}O_6$ in which holes are expected to be doped sufficiently.
2. Experimental
Polycrystalline samples of \( RE_0.6Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_3O_{8+\delta} \) \( (RE = \text{Nd, Gd, Dy, Y, Yb and Lu}) \) were prepared by the solid-state reaction method. The partial substitution of \( \text{Sr}^{2+} \) for \( \text{Ba}^{2+} \) was done in order to extend the solid solubility limit of \( \text{Ca}^{2+} \) for \( \text{RE}^{3+} \). Stoichiometric amounts of starting materials were mixed and calcined at 890°C for 24 h in air. The calcined mixture was reground and then sintered at 890°C for 24 h in air twice. Then, the annealing with three steps was carried out as follows. In the first step (annealing 1), the sintered samples were annealed at a high temperature of 800°C in flowing gas of Ar for 24 h. Through this Ar-annealing, the solid solution of Ca is expected to be promoted through the removal of oxygen ions so as to keep the charge neutrality. In the second step (annealing 2), the samples obtained thus were annealed at a low temperature of 400°C in flowing gas of \( \text{O}_2 \) for 24 h in order to fill up oxygen vacancies induced in the previous annealing process with keeping the 123-type structure. In the third step (annealing 3), the products were annealed at 350-800°C in flowing gas of Ar for 3-6 h in order to remove \( \text{O}_{\text{chain}} \) ions.

The structural analysis was carried out by the powder x-ray diffraction using \( \text{Cu} \ K_\alpha \) radiation. The iodometric titration was carried out to estimate the oxygen content. Magnetic susceptibility measurements were performed for the powdered samples using a SQUID magnetometer in a magnetic field of 10 Oe on warming after zero-field cooling in order to determine \( T_c \).

3. Results
Figure 1 shows the powder x-ray diffraction pattern of \( \text{Lu}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{Sr}_{0.4}\text{Cu}_3\text{O}_{8+\delta} \) obtained through the annealing 3 at 350-800°C. All the samples are almost of the single phase with the \( \text{RE}-123 \) structure, though a tiny amount of \( \text{BaCu}_2\text{O}_2 \) or \( \text{BaCuO}_2 \) is included for the samples annealed above 700°C. With increasing annealing-temperature, the oxygen content has been found to decreases. The oxygen content of the sample annealed at 750°C had been estimated to be about 6.0.

![Figure 1](image_url)
Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi$ for $Lu_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta}$ obtained through the annealing 3 at 350-800°C. A single-step diamagnetic signal due to the shielding effect is observed for all samples. The value of $T_c$, defined as the onset temperature of the shielding effect, is plotted against the oxygen content $6+\delta$ in Fig. 3. The value of $T_c$ is 53 K for $6+\delta \sim 6.0$ at which $O_{\text{chain}}$ is removed almost completely. For $6.0 < 6+\delta < 6.2$, $T_c$ remains unchanged, indicating that holes doped by $O_{\text{chain}}$ ions are not supplied not to the conductive Cu(2)O2 plane but to the Cu(1) site. With increasing oxygen-content, $T_c$ increases up to 82 K at $6+\delta \sim 6.5$. This increase in $T_c$ is because the holes are doped in the Cu(2)O2 plane. That is to say, one of the reasons why $T_c \sim 50$ K for $6+\delta \sim 6.0$ is much lower than 90 K is due to the low hole concentration in the Cu(2)O2 plane. With further increasing the oxygen content, $T_c$ decreases down to $\sim 70$ K for $6+\delta \sim 6.7$ because of the overdoping of holes in the Cu(2)O2 plane.

![Figure 2](image1.png)

**Figure 2.** Temperature dependence of the magnetic susceptibility $\chi$ for $Lu_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta}$ samples obtained through the annealing 3 at various temperatures.

![Figure 3](image2.png)

**Figure 3.** Dependence of $T_c$ on the oxygen content $6+\delta$ for $Lu_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta}$ samples obtained through the annealing 3.

Figure 4 shows the powder x-ray diffraction patterns of $RE_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta}$ ($RE = \text{Nd, Gd, Dy, Y, Yb and Lu}$) before and after the annealing 3 at 750°C. All the samples before the annealing 3 at 750°C are almost of the single phase with the $RE$-123 structure, while the samples after the annealing 3 at 750°C include a tiny amount of $BaCuO_2$. The crystal structure is tetragonal for all the samples after the annealing 3 at 750°C. As listed in Table 1, their lattice parameters tend to decrease as the ionic radius of $RE$ decreases. It is found that the samples of $RE_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta}$ with $\delta \sim 0$ is obtained through the annealing 3 at 750°C.
Figure 5 shows the temperature dependence of the magnetic susceptibility $\chi$ for $RE_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta}$ ($RE = Nd, Gd, Dy, Y, Yb, Lu$) samples with $\delta \approx 0$. No superconductivity appears for larger $RE = Nd, Gd$ and $Dy$, whereas superconductivity with $T_c \approx 50$ K appears for smaller $RE = Y, Yb$ and $Lu$. The values of $T_c$ are listed in Table 1. In the present work, the maximum $T_c = 53$ K for $RE = Lu$ is considerably lower than 90 K for $REBa_2Cu_3O_7$. This may be due to the low hole-concentration in the Cu(2)O$_2$ plane, because part of holes produced by the Ca-substitution are supplied to Cu(1) also, as mentioned above. In addition, it is found that $T_c$ tends to increase and the superconducting volume

### Table 1. Ionic radius of $RE$ ion, lattice parameters, oxygen content and $T_c$ for $RE_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta}$ ($RE = Nd, Gd, Dy, Y, Yb, Lu$) samples obtained through the annealing at 750°C.

| $RE$ | $r_{RE}$ (Å) | $a$ (Å) | $c$ (Å) | $6+\delta$ | $T_c$ (K) |
|------|-------------|--------|--------|------------|-----------|
| Nd   | 1.11        | 3.882  | 11.775 | 6.06       | -         |
| Gd   | 1.05        | 3.872  | 11.699 | 6.07       | -         |
| Dy   | 1.03        | 3.859  | 11.705 | 6.05       | -         |
| Y    | 1.02        | 3.854  | 11.709 | 6.05       | 49        |
| Yb   | 0.985       | 3.841  | 11.713 | 6.01       | 49        |
| Lu   | 0.977       | 3.837  | 11.712 | 6.03       | 53        |
fraction increases as the ionic radius of \( RE \) decreases. This is presumably because holes are more supplied to the Cu(2)O\(_2\) plane than to Cu(1) with decreasing \( a\)-axis-length.

4. Conclusions
We have synthesized polycrystalline samples of \( RE_{0.6}Ca_{0.4}Ba_{1.6}Sr_{0.4}Cu_{3}O_{6+\delta} \) (\( RE = \text{Nd, Gd, Dy, Y, Yb, Lu} \)) with the \( RE\)-123 structure. No superconductivity appears for larger \( RE = \text{Nd, Gd, Dy, Y, Yb, Lu} \), while superconductivity with \( T_c \approx 50 \) K appears for smaller \( RE = \text{Y, Yb and Lu} \). In the present work, the maximum \( T_c = 53 \) K for \( RE = \text{Lu} \) is considerably lower than 90 K for \( RE\text{Ba}_2\text{Cu}_3\text{O}_7 \). This may be due to the low hole-concentration in the Cu(2)O\(_2\) plane. It has been found that holes are more supplied to the Cu(2)O\(_2\) plane than to Cu(1) with decreasing \( a\)-axis-length. The contraction of CuO(2) plane, for example, by the partial substitution of Sr for Ba may allow for the increase in \( T_c \).

Acknowledgments
This work was supported by JSPS KAKENHI Grant Number JP15K06433.

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