

# Annealing effect of the irreversibility fields in (Cu,C)Ba<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>y</sub> (n = 3 and 4)

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## Abstract

Annealing effect of the irreversibility fields ( $H_{irr}$ ) in (Cu,C)Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> ((Cu,C)-1223) and (Cu,C)Ba<sub>2</sub>Ca<sub>3</sub>Cu<sub>4</sub>O<sub>y</sub> ((Cu,C)-1234) have been investigated. The samples prepared under high pressure were post-annealed in nitrogen gas in the temperature range of 400 - 500 °C.  $H_{irr}$  of (Cu,C)-1234 was improved after annealing at 450 °C while  $T_c$  remained almost constant. This suggests that carrier density of 5-coordinated CuO<sub>2</sub> planes or conductivity of charge reservoir layers is changed by annealing while keeping that of 4-coordinated CuO<sub>2</sub> planes almost constant. Both samples show  $H_{irr} \simeq 4$  T at 90 K by the post-annealing, which is quite attractive for practical application.

*Key words:* (Cu,C)-1223; (Cu,C)-1234; annealing effect; irreversibility field; high-pressure synthesis;

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## 1. Introduction

MBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (M = Y and Rare earth), which is regarded as a member (n = 2) of Cu-12(n-1)n system [1], is known to have high  $H_{irr}$  due to low anisotropy. Its research for application such as tape and bulk is developed well. (Cu,C)Ba<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>y</sub> (n = 3 and 4) [2], which is also a member of Cu-12(n-1)n system, can be considered to be a material which combines high  $T_c$  ( $\simeq 120$  K) and low anisotropy. Therefore, the possibility of application at the higher temperature ( $\geq 77$  K) is expected.

Previously, we studied annealing effect of (Cu,C)-1223 and demonstrated that (Cu,C)-1223 has a  $H_{irr}$  of 9.4 T at 77 K [3]. In this paper, we will show annealing effect of (Cu,C)-1234 as well as of (Cu,C)-1223. (Cu,C)-1223 and 1234 have crystallography inequivalent CuO<sub>2</sub>

planes. The NMR study showed that charge distribution among the CuO<sub>2</sub> planes is quite inhomogeneous so that in the case of (Cu,C)-1234 nearly optimal doped four-coordinated CuO<sub>2</sub> planes sustain an overall  $T_c$  ( $\geq 117$  K) while heavily overdoped five-coordinated ones seem to have a lower  $T_c$  ( $\geq 60$  K) [4].

We expected that  $H_{irr}$  would be increased if the carrier distribution and concentration could be controlled by annealing.

## 2. Experimental

Precursors for (Cu,C)-1223 and 1234 having the nominal compositions of Ba<sub>2</sub>Ca<sub>1.6</sub>Cu<sub>3.5</sub>O<sub>y</sub>C<sub>x</sub> and Ba<sub>2</sub>Ca<sub>2.7</sub>Cu<sub>4.6</sub>O<sub>y</sub>C<sub>x</sub> were prepared from a mixture of BaCO<sub>3</sub>, CaCO<sub>3</sub> and CuO powders at 880 °C for 24 hours in flowing oxygen gas with one in-

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intermediate grinding. The residual carbon concentration  $x$  in both the precursors was estimated to be about 0.1 by infrared absorption method. One mol of the precursors were mixed with 0.4 and 0.3 mol of  $\text{CaCO}_3$  and 0.52 and 0.4 mol of  $\text{AgO}$  (as an oxidizing agent) for sample preparation of  $n = 3$  and 4, respectively. The mixtures with nominal compositions of  $(\text{Cu}_{0.5}\text{C}_{0.5})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  and  $(\text{Cu}_{0.6}\text{C}_{0.4})\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_y$  were sealed in gold capsules and heated at 960 °C for 4 hours and at 980 °C for 2 hours under 3.5 GPa, respectively, by means of a cubic-anvil-type apparatus (RIKEN CAP-07).

The samples were ground into powders and post-annealed in a nitrogen gas flow in the temperature range of 400 - 500 °C for 12 hours. Magnetic hysteresis loops were measured with a SQUID magnetometer (MPMS-XL Quantum Design) up to 7 T. Critical current density ( $J_c$ ) was calculated by using Bean's critical state model (grain size of 7.5  $\mu\text{m}$  was used).  $H_{irr}$  was estimated from the field dependence of  $J_c$  ( $J_c = 1000 \text{ A/cm}^2$  was used as a criterion).

### 3. Results and discussion

The X-ray diffraction patterns for (Cu,C)-1223 and 1234 showed nearly single phase. EDX analysis revealed that there is no Ag in the grain.

Figure 1(a) shows the temperature dependence of  $H_{irr}$  for (Cu,C)-1223. The  $T_c$  and irreversibility line are increased with the annealing temperature. In the previous report [3], we demonstrated that there exists an optimal annealing temperature (carrier concentration) to enhance  $H_{irr}$  lines. The sample annealed at 500 °C ( $T_c = 118 \text{ K}$ ) that is slightly overdoped state shows the  $H_{irr}$  of about 3.9 at 90 K and 6.2 T at 85 K. The  $H_{irr}$  at 77 K estimated by extrapolation is 9.8 T. These values are higher than the previously reported ones [3] because the carrier concentration would be much more optimized.

Figure 1(b) shows the temperature dependence of  $H_{irr}$  for (Cu,C)-1234. Unlike (Cu,C)-1223, the  $T_c$  is almost independent of annealing temperature (only 1 K decreased). The  $H_{irr}$  line, however, once decreased by annealing at 400 °C and increased by annealing at 450 °C suggesting that there exists an optimal annealing temperature to enhance  $H_{irr}$  lines like (Cu,C)-1223. The carrier concentration of the four-coordinated  $\text{CuO}_2$  planes must be almost constant because  $T_c$  is not affected by annealing. The  $H_{irr}$  is known to depend on conductivity of charge reservoir layers as well as carrier concentration. The change of  $H_{irr}$  in (Cu,C)-1234 would result from that of carrier concentration of the five-coordinated  $\text{CuO}_2$  planes and/or the charge reservoir layers ( $\text{BaO}-(\text{Cu,C})\text{O}_y\text{-BaO}$ ). Both samples

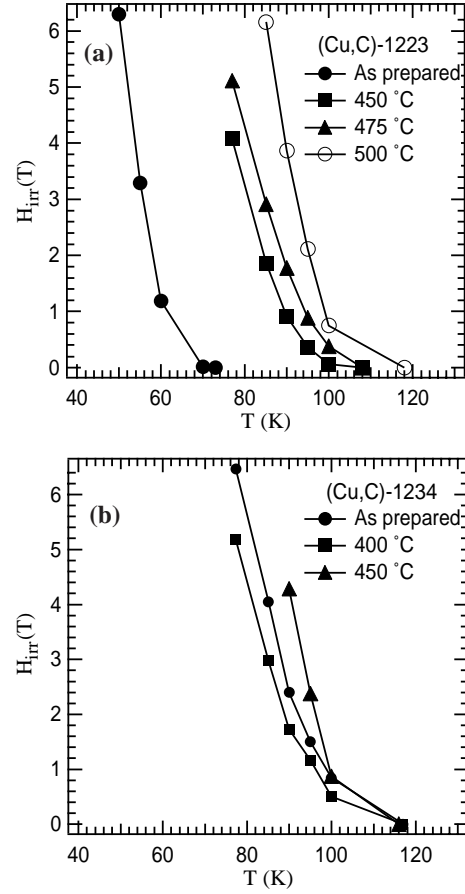


Fig. 1. Temperature dependence of irreversibility fields for (Cu,C)-1223 (a) and 1234 (b) as a function of annealing temperature.

of (Cu,C)-1223 and 1234 show a  $H_{irr}$  of about 4 T at 90 K which  $\text{YBa}_2\text{Cu}_3\text{O}_y$  ( $T_c \sim 92 \text{ K}$ ) never achieved.

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