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Anomalous oxygen annealing effects on (Cu,C)-1223

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(Cu,C)-1223 phase superconductors [$(Cu,C)Ba_2Ca_2Cu_3O_x$] consist of $(Cu,C)Ba_2O_{4-x}$ block as charge reservoir layer and three CuO_2 planes. A critical temperature (Tc) is 70K in an as-prepared sample due to synthesis condition with highly oxidized atmosphere. After reduction annealing, Tc rises up to 120K because of optimization of carrier concentration, A reversible oxygen absorption and desorption is observed with varying Tc from 86K to 120K.
An anomalous magnetization vs. temperature behavior was observed during oxygen annealing into optimal doped (Cu,C)-1223. Oxygen annealing above 500C for 1h duration, Tc fell to 96K with single transition. On the other hand, oxygen annealing below 450C, M-T curves indicated two-step transition with kink. As elongthend annealing, Tc onset is constant at 118K, kink shifted to lower temperature. More elongthend annealing, Tc is 96K with single transition. We investigated anomalous behavior of Tc during reduction and oxidization annealing.
Key words: (Cu,C)-1223, annealing, two step transition, intra grain

1. INTRODUCTION

Cuprate superconductors consists of CuO_2 plane, which carry superconductivity, and charge reservoir layer (CRL), which provide carrier to CuO_2 plane. Due to a carrier doping to CuO_2 plane, superconductivity is occurred at appropriate carrier concentration. Highest superconducting critical temperature (Tc) is realized at optimal doping. In under doped state a cuprate behave as antiferromagnetic , and in over doped state it behave as metal. In both case Tc is lowing.

(Cu,C)-system superconductors [$(Cu,C)Ba_2Ca_{n-1}Cu_nO_x$, n=3,4,5...] consist of $(Cu,C)Ba_2O_{4-x}$ block as CRL and more than three CuO_2 planes. They synthesized under high pressure condition with GPa order. Tc depends on an oxygen contents in CRL. Highest Tc of n=3, n=4 and n=5 system is 120K, 117K and 94K, respectively [1-4].

In cuprate superconductors with n>3, there are two different CuO2 planes. One is an outer plane (OP) with pyramidal oxygen coordinate, and another is an innner plane (IP) with square oxygen coordinate. Many cuprate superconductors , as Bi-system, Tl-system, Hg-system..., are same carrier concentration between OP and IP. In (Cu,C)-1234 phase different carrier concentration between OP and IP was observed by the results of NMR and specific heat [5,6].

$(Cu,C)Ba_2Ca_2Cu_3O_x$ ((Cu,C)-1223) posses three CuO_2 layers, i.e. two OP and one IP. Tc varies from 70K of as-prepared sample with heavily over doped to 120K of optimal doped sample. A difference of carrier concentration between OP and IP is not observed in (Cu,C)-1223. Then we can deal as same oxygen concentration in three planes.

Oxygen annealing is performed to the optimal doped (Cu,C)-1223, Tc fell due to over doping. Although in the case of reduction annealing from as-prepared sample Tc changes continuously with single transition [7], in the case of oxygen annealing of optimal doped sample Tc changes discontinuously with two-step transition. In this paper we investigate anomalous behavior of Tc during reduction and oxide annealing.

2. EXPERIMENTAL

Samples of (Cu,C)-1223 were synthesized under high pressure condition using cubic anvil apparatus. Appropriates amounts of BaCaCuO, CaO, CuO, and AgO, which acts as oxidizer, were mixed and reacted under a pressure of 5GPa, temperature of 1100C for 4h. Details of the sample preparation are described elsewhere [8].

Reduction annealing in N_2 flow and oxidization annealing in O_2 flow was performed using a TG/DTA apparatus with monitoring thermo gravity (TG) and differential thermal analysis (DTA). The rate of the temperature rise was 5 K/min and cooling was a furnace cooling. The optimal doped sample was prepared as follow, as-prepared sample with Tc of 70K was reduced in N_2 flow at 525C for 12h. The Tc of optimal doped sample is 120K.

Tc was determined by behavior of magnetization vs temperature curve (M-T curve). M-T curve was measured using by SQUID magnetometer (Quantum design MPMS-XL) under a field of 10Oe in zero field cooling.

3. RESULTS

3-1 Behavior of magnetization vs temperature

The M-T curve of as-prepared sample reduced in N_2 flow is shown in Fig.1. With rising an annealing temperature, Tc risen monometry with single transition.

The M-T curve of optimal doped sample annealed in O_2 flow is shown in Fig.2. Fig.2a shows the M-T curve of annealed at 500C. Tc lowered at 92K for 1h annealing, and Tc was saturated at 86K for 4h. For long time annealing more than 1h, M-T curve indicates single transition. While M-T curves indicate two step transition for short time annealing of 10 and 20min. Fig.2b shows the M-T curve of annealed at 400C. For initial stage of annealing, both transition of 118K and kink at 105K was observed. Elongthened annealing duration, kink sift to lower temperature, but transition at 118K was fixed. For 10h annealing, transition of 118K was disappeared and transition at 100K became a sole transition.

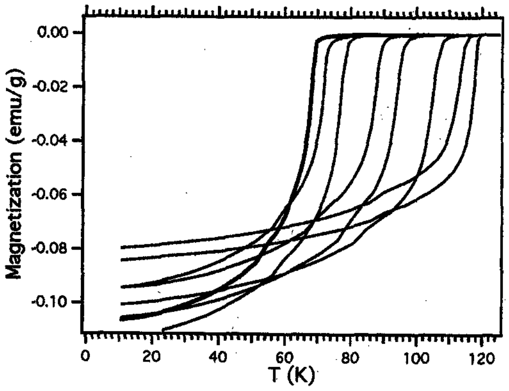

Fig.1: M-T curve of as-prepared sample reduced in N_2 flow. Bold line indicates as-prepared sample. Solid lines indicate annealed samples at 350, 400, 450, 470,490, 510 and 530C from left to right.

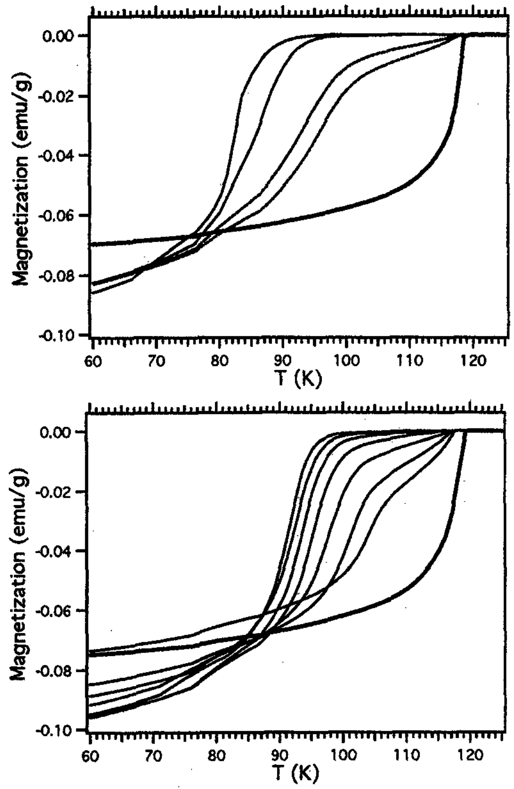

Fig.2: M-T curve of optimal doped sample annealed in O_2 flow. (a) Annealed at 500C. Dotted lines indicate annealed for 10 and 20 min from right to left. Solid lines indicate annealed for 1 and 4 h from left to right. (b) Annealed at 400C. Solid lines indicate annealed for 1, 2, 4, 6, 8, 10 and 12 h from right to left.

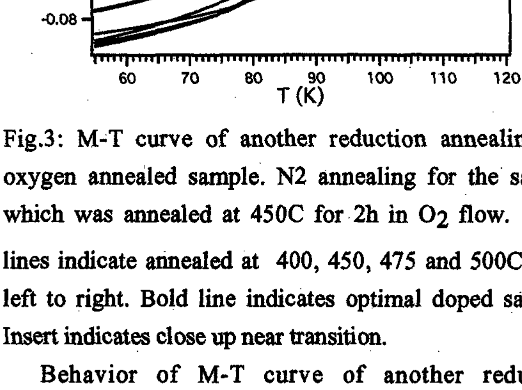

Fig.3: M-T curve of another reduction annealing for oxygen annealed sample. N2 annealing for the sample which was annealed at 450C for 2h in O_2 flow. Solid lines indicate annealed at 400, 450, 475 and 500C from left to right. Bold line indicates optimal doped sample. Insert indicates close up near transition.

Behavior of M-T curve of another reduction annealing for oxygen annealed sample is as follow. In the case of sample with fully oxygen doped under an 1 atm condition, rising reduction annealing temperature, M-T curves behave continuous change of Tc with single transition like as as-prepared sample. Fig.3 shows the M-T curve for oxygen annealed at 450C for 2h. This sample indicates two step transition, the transition at 118K and the second transition at 100K. For reduction annealing at below 400C, M-T curves indicate two step transition like as previous sample. For reduction annealing at 450C, transition at 118K is decreased and tend to single transition. For reduction annealing at 475C, M-T curve indicate single transition with Tc of 110K.

In order to clarify a behavior of kink, Fig.4 shows ΔM/ΔT-T curves of annealed at 400C. The transition at 118K don't move, although the intensity is decreased. The lower transition point appeared at 106K for 1h annealing. With elongthned the annealing duration, it shift to lower temperature and its intensity increased. For 4h annealing, the transition at 118K disappeared and one at 96K exited solely. For more elongated annealing, the transition shift to lower temperature and became 92K for 12h annealing.

3-2 Weight change

Weight change during oxygen annealing is listed in Table 1. Due to oxygen absorption weight gain is observed. Comparing between annealed at 350C and 400C, M-T curves of annealed at 350C for 24h and one at 400C for 2~3h indicate nearly same behavior. Weight change of annealed at 350C and 400C is 0.49% and 0.45~0.57%, respectively. Comparing between annealed at 400C and 500C, Tc of annealed at 400C for 12h is 94K, which is higher than Tc of 92K of annealed at 500C 1h. Although oxygen absorption of annealed at 400C is smaller than 500C view point of Tc, weight change of annealed at 400C and 500C is 1.19% and 0.51%, respectively.

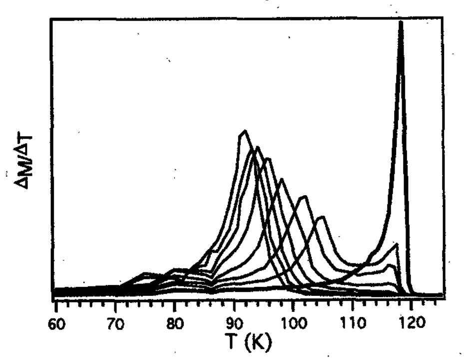

Fig.4: ΔM/ΔT-T curve of optimal doped sample annealed at 400C in O_2 flow. Solid lines indicate annealed for 1, 2, 4, 6, 8, 10 and 12 h from right to left. Bold line indicates optimal doped sample.

4. DISCUSSIONS

From the experimental results, (Cu,C)-1223 behave a single transition when reduction anneal from over doped state, and a two step transition when initial stage of oxygen anneal from optimal dope. In two step transition, one transition is constant at 118K with decreasing intensity, and another transition shift to lower temperature with increasing intensity. Because this trendy is observed in different annealing condition, it is intrinsic in (Cu,C)-1223. In this section, we discuss essential of two step transition.

4-1 Order of deviation

The reason of two step transition is thought as follow. A deviation between Cu and C in same ab-plane with removable oxygen cause a one of oxygen distribution. Then the deviation of oxygen cause an imhomogenity of carrier concentration.

Three type of imhomogenity of carrier concentration is thinkable. One is the deviation between Cu and C among crystal grain (inter grain). Next is the deviation of carrier between CuO_2 planes. As mentioned before, in multi layer cuprate superconductors two type of CuO_2 plane exists, i.e. OP and IP. Different carrier concentration between OP and IP is predicted by theoretically [9] and realized in (Cu,C)-1234. In this case, a difference between OP and IP became larger when the carrier concentration increase [10]. In (Cu,C)-1223, two step transition, occurred at slightly over doped region, and at heavy over doped

Table 1: Weight change during oxygen annealing.

annealing condition	weight change (%)
350C 6h	0.336
350C 12h	0.444
350C 18h	0.466
350C 24h	0.493
400C 2h	0.454
400C 3h	0.570
400C 6h	0.871
400C 12h	1.185
500C 1h	0.514
500C 4h	0.682

region only single Tc exists. This is contrary to the case of (Cu,C)-1234. The two step transition isn't caused by difference of carrier concentration between OP and IP. Last is charge imhomogenity in CuO_2 plane. This is caused by deviation between Cu and C in crystal grain (intra grain). A deviation less than coherent length to ab-plane isn't affect on Tc. A deviation with order of more than 10nm can affect of imhomogenity of carrier density, i. e. different Tc.

Which deviation, inter grain or intra grain, is essential? Then we discussed in comparing to experimental results. In Fig. 3 a sample with two step transition became single transition by reduction annealing. In order to appear this phenomenon, it is necessary to oxygen re-distribution during annealing. It is hardly to think movement of oxygen beyond crystal grain. Then deviation of Cu and C is order of intra grain.

4-2 Behavior of ΔM/ΔT-T

Next we discuss a behavior of ΔM/ΔT-T curve. In the case of (Cu,C)-1223, under doped state don't appears by annealing in 1 atm N_2 flow. From this fact oxygen contents in (Cu,C)-1223 is stable at optimal dope. In reduction annealing from over to optimal, oxygen leave uniformly. On the other hand, in oxidization annealing from optimal to over, oxygen

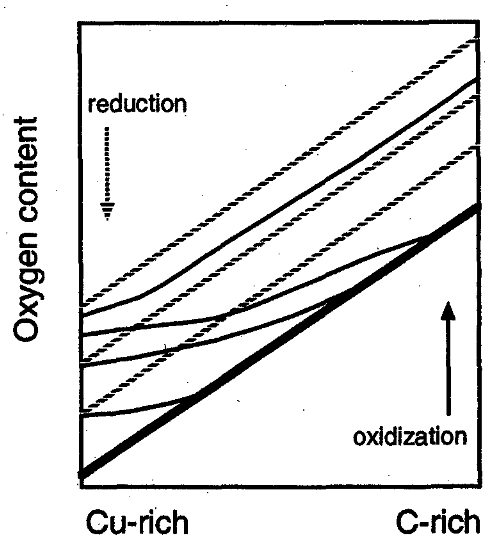

Fig.5: Schematic diagram of oxygen contents with varying Cu:C ratio. Bold line indicates optimal doped with uniform carrier concentration. Solid and dotted lines indicate oxidization and reduction annealing, respectively.

firstly introduce priority site. If there is deviation of Cu:C ratio, less oxygen exit in Cu-rich region with uniform carrier concentration. At initial stage of oxidization, oxygen priority introduce into Cu-rich region and lower temperature peak of ΔM/ΔT-T curve appears. As the oxidization progressed, oxygen gradually introduced to C-rich region. Finally oxygen distributed in proportion to Cu:C ratio with uniform carrier concentration. (Fig.5) The ratio of Cu:C varies continuously. In reduction from the state with two step transition, oxygen is re-distributed with uniform carrier concentration.

5. SUMMARY

We investigated anomalous behavior of Tc during reduction and oxidization annealing. In reduction annealing, Tc changed continuously with single transition. In oxidization annealing, two step transition observed at initial stage. The two step transition is thought to arize from deviation of Cu:C ratio in intra grain.

References

[1] H. Ihara, K. Tokiwa, H. Ozawa, M. Hirabayashi, A. Negishi, H. Matuhata, Y. S. Song, Jpn. J. Appl. Phys. 33, L503 (1994).

[2] X.-J. Wu, S. Adachi, C.-Q. Jin, H. Yamauchi, S. Tanaka, Physica C 223, 243 (1994).

[3] M.A. Alario-Franco, C. Chaillout, J.J. Capponi, J.L. Tholence, B. Souleite, Physica C 222, 243 (1994).

[4] T. Kawashima, Y. Matsui, E. Takayama-Muromachi, Physica C 224, 69 (1994).

[5] Y. Tokunaga, K. Ishida, Y. Kitaoka, K. Asayama, K. Tokiwa, A. Iyo, H. Ihara, Phys. Rev. B 61, 9707 (2000).

[6] Y. Tanaka, A. Iyo, N. Shirakawa, M. Ariyama, M. Tokumoto, S. I. Ikeda, H. Ihara, Physica C 357-360, 222 (2001)

[7] Y. Kodama, A. Iyo, M.Hirai, H. Kito, Y. Tanaka, Physica C 392-396, 77 (2003).

[8] M. Hirai, A. Iyo, H. Kito, A. Crisan, K. Tokiwa, T. Watanabe, J. Arai, Y. Tanaka, Physica C 388-389, 427 (2003).

[9] M. Mori, T. Tohyama, S. Maekawa, Phys. Rev. B 66, 064502 (2002).

[10] H. Kotegawa, Y. Tokunaga, K. Ishida, G.-g. Zheng, Y. Kitaoka, H. Kito, A. Iyo, K. Tokiwa, T. Watanabe, H. Ihara, Phys. Rev. B 64, 064515 (2001).

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