Zone-melting Process of NdBaCuO under Low Oxygen Pressure

Soh Deawha*
Department of electronic Engineering, Myongji University, Kyonggi-do 449-728, Korea

Fan Zhanguo, Gao Weiying
School of Material Science and Metallurgy, Northeastern University, China, 110004

E-mail: dwhsoh@mju.ac.kr

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The NdBaCuO superconductor samples were zone-melted in low oxygen partial pressure (1%O_2+99%Ar). The zone-melting temperature was decreased about 120°C from 1,060°C, the zone-melting temperature in air. Thus the loss of liquid phase ($BaCuO_2$ and CuO) was reduced during the zone-melting process. The content of non-superconducting phase Nd422 in zone-melted NdBaCuO samples was clearly decreased and, therefore, the substitution of Nd for Ba was occurred. The superconductivity of zone-melted $Nd_{1+x}Ba_{2-x}Cu_3O_y$ prepared under low oxygen partial pressure was distinctively improved.

Keywords : NdBaCuO superconductor, Oxygen partial pressure, Zone-melting temperature, Nd422, Superconductivity

1. INTRODUCTION

As the radius of Nd atom is approximate to that of Ba om, there tends to exist the substitution of Nd for Ba ıring the processing of NdBaCuO, i.e. the producing of ılid solution $Nd_{1+x}Ba_{2-x}Cu_3O_y$[1]. The superconductive ınsition temperature (T_c) decreased with the increasing ılue of x. When x>0.4, $Nd_{1+x}Ba_{2-x}Cu_3O_y$ will transfer into e nonsuper- conducting tetragonal phase[2]. In order to ecrease the substitution of Nd for Ba, many authors have epared $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductors with the method melt-texture growth under low oxygen partial pressure ,000 or 100 Pa), which has greatly improved the ıperconductivity[3]. Later some authors prepared Nd-$a_2Cu_3O_y$ in air and heat-treated the samples at 950°C in Ar ɔw to suppress the substitution of Nd for Ba[4,5].

We have prepared well-oriented Nd123 superconductor by ne-melting in air. After high temperature heat treatment in r and following oxygenation, the average critical current ensity in liquid nitrogen and at zero magnetic field was from 1,000 to 5,000 A/cm^2, but rarely up to 10^4 A/cm^2. lower J_c might be due to the high zone-melting temperat of 1,050 - 1,060°C. When samples moved at h temperature in the zone-melting process, some liquid ph ($BaCuO_2$ and CuO) which was decomposed from Nd would be lost undesirably. This made the content of Nd in solidified NdBaCuO crystal up to 40 - 60%, with maximum of 70%, which might enhance the substitution Nd for Ba with increasing the value of x $Nd_{1+x}Ba_{2-x}Cu_3O_y$[6-10]. Though the samples were h treated at high temperature in Ar atmosphere, the value c decreased indistinctively. In this article, the zone-melt method under low oxygen partial pressure (1%O_2+99% was used to prepare NdBaCuO superconductor. zone-melting method in NdBaCuO superconductor has advantage to decrease the melting temperature $Nd_{1+x}Ba_{2-x}Cu_3O_y$, and it results to decrease the loss of liq phase decomposed from $Nd_{1+x}Ba_{2-x}Cu_3O_y$ and the cont of Nd422. Another advantage was that the value of x wo be greatly reduced under low oxygen partial press ording to the reference[3]. With such improvement for zone-melting the critical current density (J_c) of BaCuO superconductor was approxim-ated up to 10^4 :m^2. In this article the contents of Nd422 phase in BaCuO superconductors and correspondent J_c values re measured respectively.

2. EXPERIMENTAL

The preparation of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductor powder

\ccording to the ratio of metal atoms Nd : Ba : Cu = 1 : : 3, Nd_2O_3 (>99.99%), $BaCO_3$(>99.0%), and CuO 9.0%) were weighed and mixed with alcohol in agate :. The jars were put in the ball mill running for 12 hours. ; milled mixture was put in the oven to evaporate the ɔhol. The dried powder in the corundum crucible was :ered at 950°C for 24 hours. After cooling, the powder ; ground and pressed into pellets, and then sintered. The ıve steps were repeated for 2 - 3 times in order to produce single phase Nd123 powder. Finally the sintered ıples were ground into fine particles less than 100 μm.

Zone-melting $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductor

n this experiment, the heating element in zone- melting ıace was SiC tube. The width of high temperature zone he furnace (i.e. the melting width of samples) was 7 mm. ; solidified samples were put in long quartz tube through ich the gas mixture (1% + 99%Ar) flowed.

The samples for zone-melting were the mixture of 90% Nd123 powder and 10wt% of Nd422 powder, which e pressed under 30 MPa into a rectangle of 1 mm × 5 ı × 60 mm. The samples were solidified at 950℃ for 5 - . During the zone-melting process the moving speed of ıples was 6 mm/h. 4 samples (A, B, C, D) were cut from zone-melted NdBaCuO. Then the four samples were ealed under oxygen at 350°C for 120 hours. For the ıparison with above tests, another four samples (E, F, G, were cut from the zone-melted NdBaCuO prepared in air, these samples were heat treated in Ar at 950°C for 24 for suppressing the substitution of Nd for Ba. All of the e-melted samples were oxygenated at 350°C for 120 hrs. ıdard four-probe method was used to measure the sition temperature T_c, and MPMS-SQUID magneto- er was used for magnetization hysteresis (M-H loop). The value of J_c was calculated by Bean's model.

3. RESULTS AND DISCUSSION

3.1 Oxygenation of zone-melted NdBaCuO under lo oxygen partial pressure

The oxygenation of textured $Nd_{1+x}Ba_{2-x}Cu_3O_y$ w: reported by various different references[5,6] in temperatur and normally they were 200 - 300°C. The difference mig be caused by the different sizes of samples. In order to g rid of the influence of the size factor, oriented zone-melt samples of same size were prepared. The samples with tl same size were put at different temperature zones, f example, 200, 250, 300, 350, and 400°C in the same furna through which a constant Ar flowed. The relations betwe weight increase of samples and time at differe temperatures were showed in fig. 1.

It can be seen that the optimum oxygenation temper ture for NdBaCuO was 350°C. The same results (optimum oxygenation temperature were obtained whic was approximately 100°C higher than that of sintere samples. Also the speed of oxygen flow had large effect c the increase of the oxygen content.

3.2 Melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ under lo oxygen partial pressure atmosphere

T.B. Lindemer, et al. have defined the relationship amon melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconducto oxygen partial pressure and the value of x as:

$$\log(P[O_2][MPa]) = 33.82 - 17.9x + (-48{,}226 + 24{,}983x)/T.$$

The melting temperatures of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ with differe values of x and oxygen partial pressures were calculate

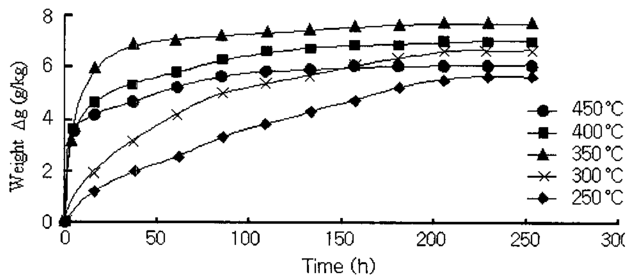
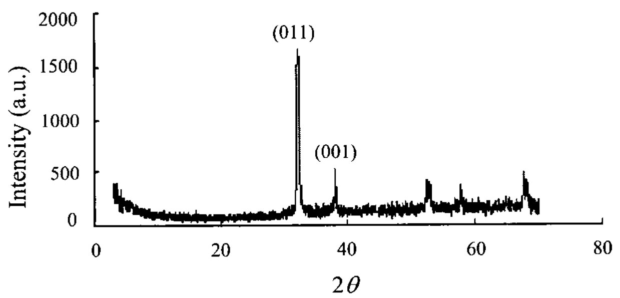


Fig. 1. Weight variation of zone-melted samples wi different oxygen absorption time.

ccording to the above formula and listed in table 1. As ıble 1 revealed, with the increasing of the value of x, the ıelting temperature tends to decrease slightly. For xamples when the value of x raised from 0 to 0.2, the ıelting temperature dropped only 1.2°C in pure oxygen tmosphere, 9.3°C at oxygen partial pressure of 0.01 MPa, nd 12.6°C at oxygen partial pressure of 0.001 MPa. Iowever, the oxygen partial pressure affected the melting emperature relatively great. When it decreased from ure oxygen down to 0.01 MPa, the melting temperature f $Nd_{1+x}Ba_{2-x}Cu_3O_y$ dropped about 75 ℃. When Id$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ was zone-melted in air, the melting emperature was 1,060°C or so, it was 1,084.7°C based on .indemer's formula. However, if the oxygen partial pressure /as 0.001 MPa, the experimental zone-melting tem- erature was about 940°C, which is 120°C lowered from ,060°C of zone-melting tem- perature in air. The large ecreasing of melting temperature caused the decreasing f flow ability of liquid phase in the melting zone, which /as decisive to the loss of liquid phase. Therefore, the ontent of Nd_2BaCuO_5 (Nd422) phase in solidified Id$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ matrix would be decreased. So, it could ontribute to the high critical current density of zone-melted IdBaCuO superconductor.

'able 1. Melting temperature (K) of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ amples, which have several x values with different oxygen ıressures.

	x				
Oxygen Pressure(Pa)	0	0.05	0.10	0.15	0.20
10^5	1,385.0	1,384.7	1,384.4	1,384.1	1,383.8
10^3	1,309.8	1,307.6	1,305.4	1,303.0	1,300.5
10	1,275.1	1,272.2	1,269.2	1,265.9	1,262.5



'ig. 2. XRD analysis of NdBaCuO superconductor pre- ›ared by zone-melting method.

3.3 Orientation of zone-melted NdBaCuO

The XRD of sample was showed as fig. 2. It was obv that the maximum diffraction of grain face was (011), al which direction the sample grew. But in the anisotı $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductor, the super-conducti along a-b plane was better than that along other faces.

Therefore, it was disadvantage to improve J_c if gr grew along (011) compared with (001) expected. Tl barely existed (001) diffraction peak in fig. 2. The g orientation of sample during zone-melting attached muc the distribution of temperature field, while the tempera field of SiC tube generating heat could hardly be change once, and it was processed and fixed.

3.4 Superconductivity

The superconductivity of NdBaCuO zone-melted in oxygen partial pressure atmosphere, the content of Nc and melting temperature correspondent were listed in t 2, and those of NdBaCuO zone-melted in air were liste table 3.

When comparing the data in the two tables, it was c that the melting temperatures under low oxygen pa pressure were lower about 120°C than those NdBaCuO zone-melted in air, either were the content Nd422 phase of samples.

But we could not figure out the optimum conten Nd422 responsible for good superconductivity. Zero resist

Table 2. Experimental results of NdBaCuO super ductor prepared by zone-melting method in air.

Samples	Melting temp. (°C)	Nd422 content (%)	T_{c0}	ΔT(K)	J_c(A/cı
E	1,050	37.9	94	2	5,10
F	1,060	42.8	87.5	5	40
G	1,070	49.5	90	3	51
H	1,090	63.2	85	5	8

Table 3. Experimental results of NdBaCuO super ductor prepared by zone-melting method in low ox pressure.

Samples	Melting temp.(°C)	Nd422 content(%)	T_{c0}(K)	ΔT(K)	J_c(A/c
A	933	33.7	94	1.9	28,46
B	940	<5	90.2	2	9,461.
C	955	<5	91.2	2	12,91
D	990	58.8	90.2	2	6,506.

ɔerature T_{c0} and transition width of NdBaCuO ɜrconductor zone-melted in low oxygen partial pressure ɔsphere were somewhat improved, especially the critical ent density J_c (A/cm^2) were raised up to 28,468.6 A/cm^2 ıple A). It could be believed that the decreasing of the ɪunt of Nd422 directly meant the increasing of ɜrconducting phase. On the other hand, the contents of ł22 affect the substitution of Nd for Ba. When there was wer content of Nd422, lower Ba atoms were replaced by atoms, i.e. the value of x in $Nd_{1+x}Ba_{2-x}Cu_3O_y$ was ller, thus improving the superconductivity of samples.

4. CONCLUSION

'he low oxygen partial pressure lowered the melting perature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ about 120°C during e-melting process. It led to less loss of liquid phase CuO_2+CuO) and less content of nonsuperconducting se Nd422, which gave less opportunity of the stitution of Nd for Ba or lowered down the value of x. above factors improved the superconductivity of e-melted NdBaCuO remarkably. NdBaCuO zone-melted ɔw oxygen partial pressure atmosphere could be directly to oxygen annealing without Ar annealing procedure. optimum oxygen annealing temperature was 350°C. As distribution of temperature field was not ideal enough in ıace, the growing orientation of samples was paralleled)11), as was expectedly.

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