

Preparation of Zone-melted NdBaCuO under Low Oxygen Pressure

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Abstract

The NdBaCuO superconductor samples were Zone-melted in low oxygen partial pressure (1% O₂ + 99% Ar). The Zone-melting temperature was decreased about 120 °C from 1060°C the zone-melting temperature in air. Thus the loss of liquid phase (BaCuO₂ and CuO) was reduced during the zone-melting process. The content of non-superconducting phase Nd422 in zone-melted NdBaCuO samples was clearly decreased, so was the substitution of Nd for Ba. The superconductivity of zone-melted Nd_{1+x}Ba_{2-x}Cu₃O_y prepared under low oxygen partial pressure was distinctively improved .

Key words : Nd123 superconductor, Low oxygen partial pressure, Zone-melting temperature

1. Introduction

As the radius of Nd atom is approximate to that of Ba atom, there tends to exist the substitution of Nd for Ba during the processing of NdBaCuO, i.e. the producing of solid solution Nd_{1+x}Ba_{2-x}Cu₃O_y [1]. The superconductive transition temperature (T_c) decreased with the increasing value of x. When x>0.4, Nd_{1+x}Ba_{2-x}Cu₃O_y will transfer into the non-superconducting tetragonal phase [2]. In order to decrease the substitution of Nd for Ba, many authors have prepared Nd_{1+x}Ba_{2-x}Cu₃O_y superconductors with the method of melt-texture growth under low oxygen partial pressure (1000 Pa or 100 Pa), which has greatly improved the superconductivity [3,4]. Later some authors prepared NdBa₂Cu₃O_y in air and heat-treated the samples at 950 °C in Ar flow to suppress the substitution of Nd for Ba [5,6].

We have prepared well-oriented Nd123 superconductor by zone-melting in air. After high temperature heat treatment in Ar and following oxygenation, the

average critical current density in liquid nitrogen and at zero field was among 1000-5000 A/cm², but rarely up to 10⁴ A/cm². The lower J_c might be due to the high zone-melting temperature of 1050 °C -1060 °C. Because when samples moved at high temperature in the zone-melting process, some liquid phase (BaCuO₂ and CuO) which was decomposed from Nd123 would be lost undesirably. This made the content of Nd422 in solidified NdBaCuO crystal up to 40 % - 60 %, with the maximum of 70 %, which might enhance the substitution of Nd for Ba, i.e. increase the value of x in Nd_{1+x}Ba_{2-x}Cu₃O_y[7]. Though the samples were heat-treated at high temperature in Ar atmosphere, the value of x decreased indistinctively. In this article zone-melt method under low oxygen partial pressure (1% O₂ + 99% Ar) was used to prepare NdBaCuO superconductor. In this method one advantage was that the melting temperature of Nd_{1+x}Ba_{2-x}Cu₃O_y could be decreased, which decreased the loss of liquid phase decomposed from Nd_{1+x}Ba_{2-x}Cu₃O_y, and decreased the content of Nd422 in zone-melted NdBaCuO superconductor. The another advantage was that the value of x would be greatly reduced under low oxygen partial

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pressure according to references [3,4]. With such improvement for the zone-melting the critical current density (J_c) of NdBaCuO superconductor was up to 10^4 A/cm². In this article the contents of Nd422 phase in NdBaCuO superconductors and correspondent J_c values were measured respectively.

2. Experiment

2.1 Preparation of Nd_{1+x}Ba_{2-x}Cu₃O_y powder

According to the ratio of metal atoms Nd:Ba:Cu = 1:2:3, Nd₂O₃(>99.99 %), BaCO₃(>99.0 %), CuO(>99.0 %) were weighed and mixed with alcohol in agate jars. The jars were put in the ball mill running for 12 hours. The milled mixture was put in the oven to evaporate the alcohol. The dried powder in the corundum crucible was sintered at 950 °C for 24 hours. After cooling, the powder was ground and pressed into pellets, and then sintered. Above steps were repeated for 2-3 times in order to produce the single phase Nd 123 powder. Finally the sintered samples were ground into fine particles less than 100 μm.

2.2 Zone-melting process of Nd_{1+x}Ba_{2-x}Cu₃O_y

In this experiment, the heating element in zone-melting furnace was SiC tube. The width of high temperature zone of the furnace (i.e. the melting width of samples) was 7 mm. The solidified samples were put in long quartz tube through which the gas mixture (1% O₂ + 99% Ar) flowed.

The samples for zone-melting were the mixture of 90 % of Nd123 powder and 10 wt% of Nd422 powder, which were pressed under 30MPa into rectangle of 1 mm×5 mm×60 mm. The samples were solidified at 950°C for 5-6 h. During the zone-melting process the moving speed of samples was 6 mm/h. 4 samples (A, B, C, D) were cut from the zone-melted NdBaCuO, Then the four samples were annealed under oxygen at 350 °C for 120 h. For the comparison test, another four samples (E, F, G, H) were cut from the zone-melted NdBaCuO prepared in air, the samples E, F, G, H were heat treated in Ar at 950 °C for 24 h for suppressing the substitution of Nd for Ba. All of the zone-melted samples were oxygenated at 350 °C for 120 hours. Standard four-probe method was used to measure the transition temperature T_c , and

MPMS-SQUID magnetometer 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 low oxygen partial pressure

The oxygenation temperatures of textured Nd_{1+x}Ba_{2-x}Cu₃O_y were reported variously by different references and normally they were 200 °C -300 °C. The difference might be caused by the different sizes of samples. In order to get rid of the influence of the size factor, oriented zone-melted samples of same size were prepared. The samples with the same size were put at different temperature zones, for example, 200, 250, 300, 350, 400 °C in the same furnace, through which a constant Ar flow passed. The relations between weight increase of samples and time at different temperatures were showed in figure 1. It can be seen that the optimum oxygenation temperature for NdBaCuO was 350 °C. The same result was obtained was 100°C higher than the oxygenation temperature of sintered samples. Also the speed of oxygen flow had large effect on the increase of the oxygen content.

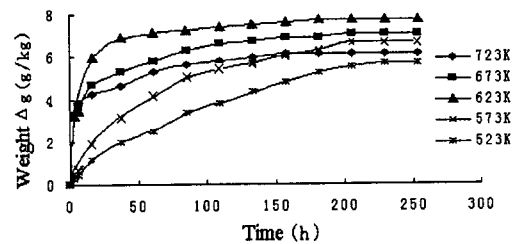


Fig. 1. Weight variation of zone-melted samples with variable oxygen absorption time.

3.2 Melting temperature of Nd_{1+x}Ba_{2-x}Cu₃O_y under low oxygen partial pressure

T. B. Lindemer et al. have defined the relationship among melting temperature of Nd_{1+x}Ba_{2-x}Cu₃O_y superconductor, oxygen partial pressure and the value of x as :

$\log (P[O_2][MPa])$

$$= 33.82 - 17.9x + (-48226 + 24983x)/T.$$

Table 1. Melting temperature (K) of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ samples which has several x value with several oxygen pressure.

oxygen pressure(Pa)	x				
	0	0.05	0.10	0.15	0.20
10^0	1385.0	1384.7	1384.4	1384.1	1383.8
10^5	1309.8	1307.6	1305.4	1303.0	1300.5
10	1275.1	1272.1	1269.2	1265.9	1262.5

The melting temperatures of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ with different values of x and oxygen partial pressures were calculated according to above formula and listed in table 1. As table 1 revealed, with the increasing of the value of x, the melting temperature tends to decreasing slightly. For example when the value of x raised from 0 to 0.2, the melting temperature dropped only 1.2 °C in pure oxygen atmosphere, 9.3 °C when oxygen partial pressure was 0.01 MPa, and 12.6 °C when oxygen partial pressure was 0.001 MPa. However oxygen partial pressure affected the melting temperature relatively great. When it decreased from pure oxygen down to 0.01 MPa, the melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ dropped about 75 °C. When $Nd_{1+x}Ba_{2-x}Cu_3O_y$ was zone-melted in air, the melting temperature was 1060 °C or so, it was 1084.7 °C based on Lindemer's formula. When the oxygen partial pressure was 0.001 MPa, the experimental zone-melting temperature was about 940 °C, which was 120 °C reduced from 1060 °C. The large decreasing of melting temperature caused decreasing of flow ability of liquid phase in the melting zone, which was decisive to the loss of liquid phase. Therefore the content of Nd_2BaCuO_5 (Nd_{422}) phase in solidified $Nd_{1+x}Ba_{2-x}Cu_3O_y$ matrix was decreased. It would contribute to high critical current density of zone-melted NdBaCuO superconductor.

3.3 Orientation of zone-melted NdBaCuO

The XRD of sample was showed as figure 2. It was obvious that the maximum diffraction of grain face was (011), along which direction the sample grew. But in the anisotropy $Nd_{1+x}Ba_{2-x}Cu_3O_y$

superconductor, the superconductivity along a-b face was better than that along other faces. Therefore, it was disadvantage to improve J_c if grains grew along (011) compared with (001) expected. While there barely existed (001) diffraction peak in figure 2. The grain orientation of sample during zone-melting attached much to the distribution of temperature field, while the temperature field of SiC tube generating heat could hardly be changed once it was processed and fixed.

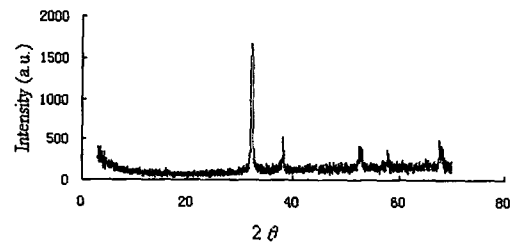


Fig. 2. XRD analysis of NdBaCuO superconductor prepared by zone melting method.

3.4 Superconductivity

The superconductivity of NdBaCuO zone-melted in air, the content of Nd_{422} and melting temperature correspondent were listed in table 2, and those of NdBaCuO zone-melted in low oxygen partial pressure atmosphere were listed in table 3.

Table 2. The experimental result of NdBaCuO superconductor prepared by zone melting method in air.

sample number	melting T (°C)	Nd422 content(%)	T_{c0} (K)	ΔT (K)	J_c (A/cm ²)
A'	1050	37.9	94	2	5100
B'	1060	42.8	87.5	5	400
C'	1070	49.5	90	3	510
E'	1090	63.2	85	5	80

When comparing the data in the two tables, it was clear that the melting temperatures under low oxygen partial pressure were lower about 120 °C than those of NdBaCuO zone-melted in air, either were the contents of Nd_{422} phase of samples. But we could not figure out the optimum content of Nd_{422} responsible for good superconductivity. Zero resistance temperature T_{c0} and transition width of

NdBaCuO superconductor zone-melted in low oxygen partial pressure atmosphere were somewhat improved, especially the critical current density J_c (A/cm²) were raised up to 28468.6 A/cm² (sample A). It could be believed that the decreasing of the amount of Nd422 directly meant the increasing of superconducting phase. On the other hand, the content of Nd422 affect the substitution of Nd for Ba. When there was a lower content of Nd422, lower Ba atoms were replaced by Nd atoms, i.e. the value of x in Nd_{1+x}Ba_{2-x}Cu₃O_y was smaller, thus improving the superconductivity of samples.

Table 3. The experimental result of NdBaCuO superconductor prepared by zone melting method in low oxygen pressure.

sample number	melting T (°C)	Nd422 content(%)	T _c (K)	ΔT (K)	J _c (A/cm ²)
A	933	33.7	94	1.9	28468.6
B	940	< 5	90.2	2	9461.7
C	955	< 5	91.2	2	12910.7
D	990	58.8	92.2	2	6506.8

4. Conclusion

The low oxygen partial pressure lowered the melting temperature of Nd_{1+x}Ba_{2-x}Cu₃O_y about 12 0°C during zone-melting process. It led to less loss of liquid phase (BaCuO₂+CuO) and less content of non-superconductivity phase Nd422, which made less opportunity of the substitution of Nd for Ba or lowed down the value of x. These factors above improved the superconductivity of zone-melted NdBaCuO remarkably. NdBaCuO zone-melted in low oxygen partial pressure atmosphere could be directly put to oxygen anneal without Ar annealing. The optimum oxygen annealing temperature was 350°C. As the distribution of temperature field was not ideal, the growing orientation of samples paralleled to (011).

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