$Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ Bulk Superconductor by Zone-melt Process

Dea-Wha Soh
Department of Electronic Engineering, Myongji University, Yongin, Kyunggi-do 449-728, Korea

Fan Zhan-Guo
Materials and Metallurgy School, Northeastern University, Shenyang 110006, P.R. China

E-mail : dwhsoh@mju.ac.kr

(Received 1 June 2002, Accepted 2 August 2002)

Two kinds of $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$, the sintering samples and zone melting samples, were heat-treated under pure Ar at 950 °C. The substitution of Nd ion for Ba ion in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ before and after the heat treatment was investigated by XRD. In order to confirm the effects of the heat treatment, the T_c and J_c of samples with/without the heat treatment under Ar were comparatively studied. The $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples were oxygenated under pure oxygen at 300 °C. From the XRD pattern it was found that the sample with $x<0.4$ was transferred from tetragonal phase to orthorhombic phase after the oxygenation, while the sample with $x>0.4$ did not show the phase transition even after a long time oxygenation. Therefore, the low oxygen partial pressure (Ar + 1 % O_2) was used for the ambient atmosphere of the zone-melting samples, which could reduce the melting temperature and depress the substitution of Nd for Ba. After the improvement in the zone-melting process, the J_c value was increased to 2×10^4 A/cm^2 (0 T, 78 K). The particle orientation and the structure of zone-melted NdBaCuO were studied by the XRD and SEM analysis.

Keywords : $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$, tetragonal phase, orthorhombic phase, oxygenation, zone-melting process

1. INTRODUCTION

$Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ solid solution compound became a promising superconductor because of its high critical current density (J_c) at high magnetic field[1,2] and its high growth speed for the textured material[3]. There are some disadvantages in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductor and its synthesis process. The first problem is the change of critical transition temperature (T_c) with the solid solubility x in the solid solution[4]. When the x value larger than 0.4 the compound become a non-superconductive tetragonal phase[5].

The substitution of Nd for Ba exists in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductor prepared in air[6-8]. Therefore some authors use low oxygen partial pressure as the ambient atmosphere for preparing $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductor in the melting-condensed process (so called OCMG) in order to depress the substitution[9,10]. Some authors prepared the textured $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductor in air, and then used a high temperature (>900 °C) heat treatment process in argon to reduce the substitution of Nd for Ba[11].

In the paper, the textured $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductor was prepared by the zone-melting process both in air and in the mixture of argon with 1 % oxygen. The samples made in air need to undergo the high temperature heat treatment in argon before the oxygenation, while the samples made in the mixed gas directly were oxygenated in pure oxygen at low temperature after zone-melting. The superconductivity (T_c and J_c) of small samples was studied and large column in the NdBaCuO superconductor of 20 mm diameter was prepared by the zone-melting process.

2. EXPERIMETAL

Two kinds of samples, sintering sample and zone melting sample, were used in the heat treatment test. Nd_2O_3 (99.9 %), $BaCO_3$ (99 %) and CuO (99.9 %) were weighted and mixed on the metal ratio of Nd : Ba : Cu = 1 : 2 : 3. The $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ powder was sintered by the powder metallurgical method. In order to obtain the single phase of $NdBa_2Cu_3O_{7-\delta}$ compound, the above sintering processing was repeated 2-3 times. The $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples with different x were sintered from the chemicals of Nd_2O_3 (99.9 %), Ba $(NO_3)_2$ (99 %) and CuO (99.9 %). The chemicals were weighted on x = 0.075, 0.25, 0.35, 0.45 and 0.85. Then those were mixed, ground and sintered individually. The process also needs to repeat 2-3 times for the single-phase compounds. For the zone-melting samples, the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ powder was pressed into 60 × 6 × 1.5 mm^3 bars which were solidified at 950 ℃ in air. A new designed SiC tube was used for the heating element, which could have a narrow high temperature zone. Because the zone melting was taken in the air, Nd ion would take some Ba ion site to form the substitution of Nd for Ba. After the zone-melting in air, the sample was heat treated in pure Ar at 950 °C to reduce the substitution. After the Ar heat treatment, the zone-melting samples were oxygenated at 300 °C for 120 hours under pure oxygen flow. The Ar heat treatment and the oxygenation were taken in the same SiC furnace. The standard four-probe method was used to measure T_c and J_c. The four Ag electrodes for the measurements were coated before the heat treatment. The details for the preparation and the measurements of samples were shown in reference[12].

3. RESULTS AND DISCUSSION

For the sintering samples of $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ with different x, the XRD was taken before and after the oxygenation, and the patterns presented between 2θ = 57.5° and 2θ = 58.5° were shown in fig. 1. When x was smaller than 0.4, after oxygenation the diffraction peak moved to the right, which showing the transition from tetragonal to orthorhombic. When x was larger than 0.4, the diffraction peak did not change its position after the oxygenation. It means that with the increasing substitution of Nd for Ba (x>0.4) it is difficult to make the samples of $NdBa_2Cu_3O_{7-\delta}$ transfer from tetragonal to orthorhombic by means of the oxygenation. When the content of $Nd_4Ba_2Cu_2O_{10}$ (Nd422) phase is smaller than 5 %, it is difficult to prepare the well-oriented samples in air by zone-melting.

Therefore, the bars of $NdBa_2Cu_3O_{7-\delta}$ for zone-melting was mixed with 10-15 % Nd422 phase in order to make well oriented samples. The measured Nd422 contents after zone melting are higher than 40 %. T_c of zone-melted bars is lower than that of sintering ones, and J_c is small even for the well-oriented NdBaCuO samples, which may due to the increased x value with the increaseing Nd422 phase. Therefore, the suitable Nd422 content is one of the important factors in the preparation of high J_c $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$.

Weight changes of NdBaCuO superconductor (12.0 × 4.5 × 3 mm^3) at different times on oxygen absorption was shown in fig. 2. It was demonstrated that the optimal oxygen absorption was at 250 °C in the samples of $NdBa_2Cu_3O_{7-\delta}$. A typical XRD pattern for zone-melting NdBaCuO was shown in fig. 3, in which the X-ray was vertical to the pulling direction of sample.

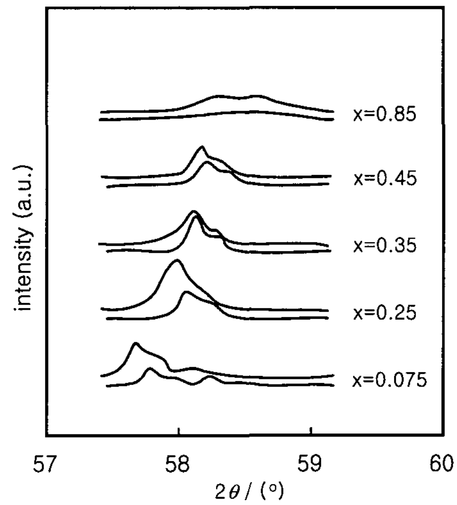

Fig. 1. XRD patterns of samples with varies x before and after oxygenation (below line is the one after oxygenation for each group).

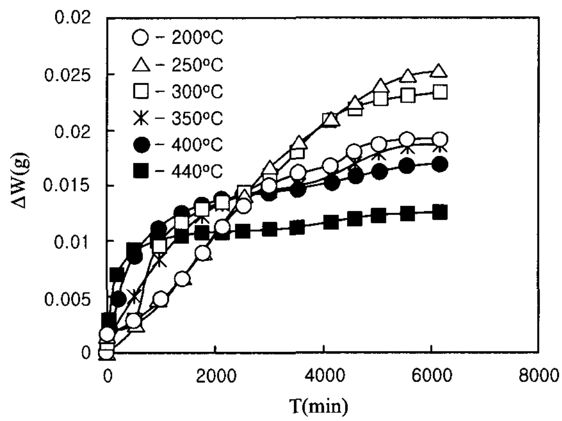

Fig. 2. Weight changes of NdBaCuO samples (12.0 × 4.5 × 3 mm^3) during oxygen absorption process.

Table 1. The effect of Ar post heat treatment on superconductivities.

Post heat Treatment	Sintered $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$			Zone-melted $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$
	$T_{c,onset}$	$T_{c,offset}$	J_c (A/㎠)	J_c (A/㎠)
Without Ar	89.5K	82K	3	24
With Ar	94.5K	89K	15	100

Table 2. J_c and Nd422 content of textured NdBaCuO.

Nd422 (wt%)	73.74	33.89	32.71	29.98	25.08	17.12	15.00	13.00
J_c (A/㎠)	27	35	40	100	3100	5400	20700	12900

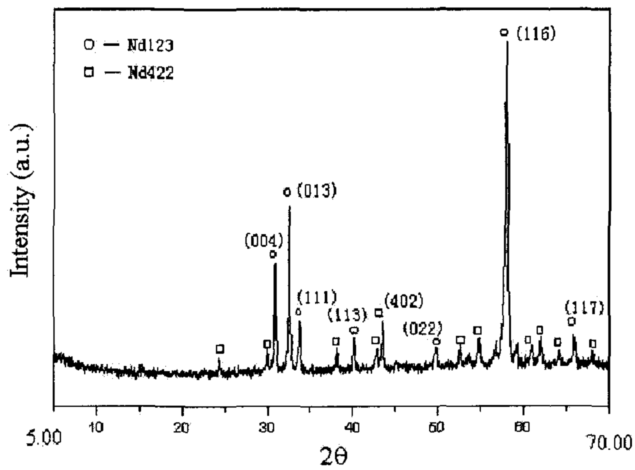

Fig. 3. XRD pattern of zone-melted NdBaCuO.

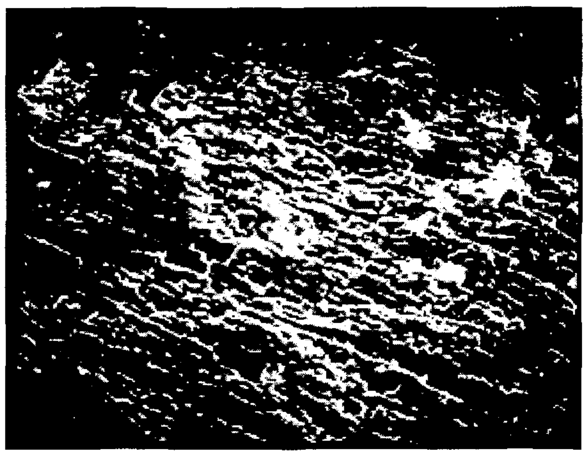

Fig. 4. Microstructure of zone-melted NdBaCuO.

In figure 3, it can be seen that there is a strong diffraction peak on the (116) crystal plane. The microstructure of cross section on oriented sample is as shown in fig. 4.

The heat treatment at 950 °C under Ar is effective for the improvement of superconductivity of NdBaCuO. The comparative data of T_c and J_c with and without Ar heat treatment were listed in table 1. The critical transition temperature (T_c) increased 5-7 K for the samples with Ar heat treatment, and J_c increased 5 times.

Although Nd422 phase is useful for the preparation of textured $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductor, the excessive content of it may reduce the ability of current transportation. After the Nd422 phase content in the textured NdBaCuO samples was adjusted, the J_c values was increased up to 2×10^4 A/cm^2 (0 T, 78 K) (see table 2).

The main factor of adjustment of Nd422 phase content is melting temperature in the process of textured NdBaCuO superconductor. In the test low oxygen partial pressure was used as the ambient atmosphere, which could reduce the melting temperature of about 100 °C. Therefore, the loss of liquid phase ($BaCuO_2$ and CuO) and the Nd422 content would be reduced. It means the low oxygen partial pressure was effective to depress the liquid phase and Nd422 contents of NdBaCuO system. The substitution of Nd for Ba is another important role for improvement of superconductivity.

4. CONCLUSION

Both sintering and zone-melted NdBaCuO samples could be made in air existing the substitution of Nd for Ba, namely x>0 in $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. But the substitution could be reduced by the heat treatment in pure Ar at 950 °C, so the superconductivity could be improved by this process. When x>0.4 in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ samples, it could not be transferred from tetragonal to orthorhombic phase even after a long time oxygenation. However, addition of Nd422 in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ bar could increase the x value after zone-melting. It was found that the optimal temperature and time of oxygen absorption were 250 °C and 6000 min, respectively.

The textured NdBaCuO superconductor was prepared by the zone-melting method in air. After zone-melting, the NdBaCuO samples were heat-treated at high temperature (900-950 °C) in Ar. The high melting point of NdBaCuO sample caused the loss of liquid phase ($BaCuO_2$ and CuO) in the zone-melting process. Therefore, higher Nd422 content may reduce the critical current density of the samples. When the low oxygen pressure was used in the zone-melting process, the melting temperature of NdBaCuO was reduced. The J_c value of the zone-melted sample after the post heat treatment increased up to 2×10^4 A/cm^2 (0 T, 78 K).

ACKNOWLEDGMENTS

This work was accomplished by KISTEP grant of M1-0011-00-0043 for Int'l. Joint-Research Program.

REFERENCES

[1] M. Murakami, S. Yoo, T. Higuchi, N. Sakai, J. Welts, N. Koshizuka, and S. Tanaka, "Flux pinning in melt-grown $NdBa_2Cu_3O_y$ and $SmBa_2Cu_3O_y$ superconductors", Jpn. J. Appl. Phys., Vol. 33, No. 5B, p. 715, 1994.

[2] S. I. Yoo, N. Sakai, H. Takaichi, and M. Murakami, "Melt processing for obtaining $NdBa_2Cu_3O_\gamma$ superconductors with high T_c and large J_c", Appl. Phys. Lett., Vol. 65, No. 5, p. 633, 1994.

[3] K. Salama and A.S. Parikh, "High rate melt texturing of $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ type superconductors", Appl. Phys. Lett., Vol. 68, p. 1993, 1996.

[4] T. Plackowski, C. Sułkowski, D. Włosewizs, and J. Wnuk, "Effect of the RE^{3+} ionic size on the $REBa_2Cu_3O_{7-\delta}$ ceramics oxygenated at 250 bar", Physica C, Vol. 300, p. 184, 1998.

[5] J. K. Liang, G. C. Che, and S. L. Chen (eds.), "Phase relation and crystal structure of high Tc oxide superconductive system", Science Press, China, 1999, p. 196.

[6] Z. Fan, D. Soh, P. Si, Y. Li, and B. Lim, "Heat treatment condition for preparing $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductors", Proc. 2001 Summer Conf. KIEEME, p. 624, 2001.

[7] D. Soh, Z. Fan, H. Kim, W. Gao, and T. Kim, "Preparation of Zone-melted NdBaCuO under Low Oxygen Pressure", Proc. 2001 Autumn Conf. KIEEME, p. 85, 2001.

[8] Soh Deawha, Fan Zhanguo, and Gao Weiying, "Zone-melting process of NdBaCuO under low oxygen pressure", Trans. On EEM, Vol. 3, No. 2, p. 24, 2002.

[9] H. Wu, M. J. Kramer, K. W. Denis, and R. W. McCallum, "Mechanism for flux pinning in $NdBa_2Cu_3O_{7-\delta}$ melt-textured in low oxygen partial pressure", Appl. Phys. Lett., Vol. 71, No. 24, p. 3572, 1997.

[10] M. Muralidhar, S. Koishikawa, M. R. Koblischka, and M. Murakami, "Study of superconducting properties of OCMG processed (Nd, Eu, Gd)-Ba-Cu-O with Pr doping", Physica C, Vol. 314, iss. 3-4, p. 277, 1999.

[11] A. M. Hu, Z. X. Zhao, W. Gawalek, M. Wu, T. Strasser, and P. Goerner, "Preparation and character-ization of melt-textured $Nd_{1+x}Ba_{2-x}Cu_3O_y$ made in air", Physica C, Vol. 282-287, iss. 1, p. 431, 1997.

[12] P. Z. Si, Z. G. Fan, and C. W. Xu, "Zone-melted NdBaCuO superconductors", J. of the Chinese Rare Earth Soc., Vol. 18, p. 311, 2000.