

## Heat Treatment Condition for Preparing $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ Superconductors

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### Abstract

Two kinds of  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ , 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  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  before and after the heat treatment were investigated by XRD. In order to know the effects of the heat treatment, the  $T_c$  and  $J_c$  of samples with the heat treatment and those without the heat treatment by Ar were comparatively studied. The results show that the substitution of Nd for Ba decreased,  $T_c$  and  $J_c$  increased after the treatment under Ar at 950°C. The  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  samples were oxygenated under pure oxygen at 300°C. From the XRD pattern it was found that the sample with  $x < 0.4$  could transfer from tetragonal phase to orthorhombic phase after the oxygenation, but the sample with  $x > 0.4$  could not make the phase transition even after a long time oxygenation.

**Key words** : rare earth metal,  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  superconductors, heat treatment, solid solubility, superconductivity

### 1. Introduction

Compared with YBaCuO superconductor the NdBaCuO has higher critical current density ( $J_c$ ) at high field [1],  $J_c$  equals about  $1 \times 10^4$  A/cm<sup>2</sup> at 2 Tesla field for NdBaCuO but for YBaCuO it was 2000 A/cm<sup>2</sup> at the same field. NdBaCuO has higher growth speed when Bridgmen method was used to prepare the oriented material [2]. When the speed was 50 mm/h, the sample still could get high orientation for NdBaCuO, but for YBaCuO the growth speed was 1 or 2 mm/h only. Because of high critical current density and the growth characteristics, NdBaCuO was concerned one of the most promising for the development of high temperature superconductors.

In the system  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  solid solution with  $x=0$  to  $x=0.9$  can be formed,  $x$  value can be changed with the processing temperature and atmosphere [2].  $T_c$  decreases with increasing  $x$  value. When  $x$  larger than 0.4 the compound transfers to tetragonal [4]. In order to depress the substitution of Nd for Ba, some authors prepared NdBaCuO superconductor under 1% or 0.1% oxygen partial pressure [5].

Salama et al grew NdBaCuO superconductor in air by the directional solidification in a modified Bridgman furnace; Hu prepared NdBaCuO superconductor in air by the MTG method [6]. After the processing the superconducting material heat treated in pure Ar at 900~950°C for 20 hours in order to decline the substitution of Nd for Ba. The heat treatment under Ar at high temperature for the NdBaCuO materials made in air is an important processing. For the zone-melting method because of the movement of equipment, it is

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difficult to control the oxygen partial pressure. In the experiment the zone melting processing of NdBaCuO was taken in air, and then the zone melted NdBaCuO bars was heat treated in Ar at 950°C. The effects of the Ar treatment on decreasing of the replace of Nd for Ba were examined by the XRD and the measurements of superconductivity ( $T_c$ ,  $J_c$ ).

## 2. Experimental part

Two kinds of samples, sintering sample and zone melting sample, were used in the heat treatment test.  $\text{Nd}_2\text{O}_3$  (99.9%),  $\text{BaCO}_3$  (99%) and  $\text{CuO}$  (99.9%) were weighted and mixed on the metal ratio of  $\text{Nd} : \text{Ba} : \text{Cu} = 1 : 2 : 3$ . The  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  powder was sintered by the powder metallurgical method. In order to obtain the single phase  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound, above sintering processing would repeat 2~3 times. The  $\text{Nd}_{1-x}\text{Ba}_x\text{Cu}_3\text{O}_{7-\delta}$  samples with different x were sintered from the chemicals  $\text{Nd}_2\text{O}_3$  (99.9%),  $\text{Ba}(\text{NO}_3)_2$  (99%) and  $\text{CuO}$  (99.9%). The chemicals were weighted on  $x = 0.075, 0.25, 0.35, 0.45$  and  $0.85$ , and then mixed, ground and sintered. The process also needs to repeat 2~3 times for the single-phase compounds. For the zone-melting samples the  $\text{Nd}_{1-x}\text{Ba}_x\text{Cu}_3\text{O}_{7-\delta}$  powder was pressed into 60mm X 6mm X 1.5mm bars which were solidified at 950 °C 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 would be 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 [7].

## 3. Results and discussions

The sample of zone-melted  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , before and after the Ar heat treatment, and after the oxygenation was taken X-ray diffraction (XRD). The three XRD curves in the scanning angle  $2\theta = 32^\circ \sim 32.8^\circ$  were shown in figure 1. Each curve of figure 1 includes several peaks, although the strong peak covers the weak one. For zone-melted sample the strong peak is in the low angle part. After the oxygenation of the sample at 300°C the strong peak is in the high angle part. Therefore the zone-melted  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is tetragonal phase, and after the oxygenation the sample transfers to orthorhombic phase. It is noticed that after the Ar heat treatment the sample presents the orthorhombic tendency. in XRD pattern. When x value is larger than 0.4,  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is tetragonal, with the decreasing of x value, on the other word, with the decreasing of the substitution of Nd for Ba,  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  transfers to the orthorhombic.

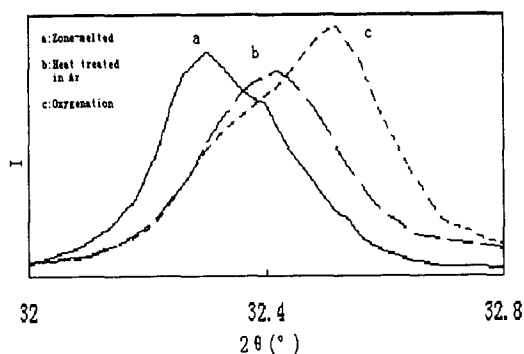


Figure 1. XRD pattern of zone-melted samples at different step of heat treatment

In figure 1 it can be seen that after the Ar heat treatment sample zone-melted in air tends to be orthorhombic, which proves Ar heat treatment can reduce the substitution of Nd for Ba. Both of Ar heat treatment and oxygenation have the effects on the  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  to tend the orthorhombic phase. In order to examine the effects of Ar heat treatment, some of the samples, both the sintering samples and zone-melted samples undergo Ar heat

treatment before the oxygenation, and some of samples only undergo the oxygenation without Ar heat treatment.  $T_c$  and  $J_c$  of measured were shown in table 1.

From table 1 it is seen that for the sintering samples after Ar heat treatment,  $T_c$  increased 5-7 times. It means that although the samples of  $NdBa_2Cu_3O_{7-\delta}$  were prepared on the ratio of Nd : Ba : Cu = 1 : 2 : 3, if sintered in air, the substitution of Nd for Ba may occur. Therefore after the Ar heat treatment superconductivity improved. For the zone-melted samples after the Ar heat treatment  $J_c$  increased about 5 times. The improvement of  $J_c$  is due to the decreasing of the substitution of Nd for Ba. The results of the superconductive measurements are in accordance with above discussion for XRD.

Table 1. Relation of the condition of heat treatment and the superconductivity

Conditions of 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	$T_c$ o	$J_c$ (A/cm <sup>2</sup> )	$J_c$ (A/cm <sup>2</sup> )
Oxygenation	89.5K	82K	3	24
Ar heat treatment and oxygenation	94.5K	89K	15	110

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  $2\theta = 57.5^\circ$  and  $2\theta = 58.5^\circ$  were shown in figure 2. When x is smaller ( $< 0.4$ ) after the oxygenation the diffraction peak moved to the right. which shown the transition from tetragonal into orthorhombic. When x is larger than 0.4, the diffraction peak did not change its position almost 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 into orthorhombic by means of the oxygenation. In the zone-melting test when the content of  $Nd_4Ba_2Cu_2O_{10}$  (Nd422) phase is smaller than 5%, it is difficult to prepared the well oriented samples in air.

Therefore the bars of  $NdBa_2Cu_3O_{7-\delta}$  for zone-melting mix 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 increasing Nd422 phase. Therefore the suitable Nd422 content is one of the important factors in the preparation of high  $J_c$   $NdBa_2Cu_3O_{7-\delta}$ .

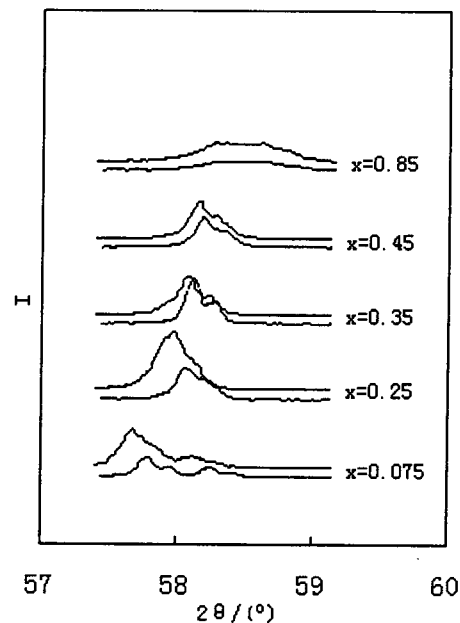


Figure 2. XRD pattern of samples with varies x before and after oxygenation (below line is the one after oxygenation for each group)

#### 4. Conclusions

Both sintering and zone-melted  $NdBaCuO$  samples was made in air existing the substitution of Nd for Ba, namely  $x > 0$  in  $Nd_{1-x}Ba_{2-x}Cu_3O_{7-\delta}$ . The substitution can be reduced by the heat treatment in pure Ar at  $950^\circ C$ , and the superconductivity can be improved. When  $x > 0.4$ , the  $Nd_{1-x}Ba_{2-x}Cu_3O_{7-\delta}$  samples can not transfer from tetragonal phase into orthorhombic phase

even after a long time oxygenation. Addition of Nd422 in the  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bar can increase the x value after zone-melting.

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### **References**

- [1] Takahama Masahide, Goto Tomoko, Watanabe Kazuo. Field dependence of  $J_c$  for melt textured filamentary  $\text{Nd}_{123}$  superconductor J. Physica C, 1998, 298: 85-90
- [2] Salama K., Parikh A. S., Woolf L., High rate melt texturing of  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  type superconductors J. Appl. Phys. Lett. 1996, 68 : 1993-1995
- [3] Goodilin E. A., Oleynikov N. N., Antipov E. V., et al. On the stability region and structure of the  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$  solid solution. J. Physica C, 1996,272: 65-78
- [4] Fu S. G., Xie X. S., Phase relation and crystal structure in the system of  $\text{Nd}_2\text{O}_3$ -BaO-CuO [J]. Ke xue tong bao, 1989, 20 : 1540-1542
- [5] Yoo S. I., Sakai N., Takaichi H., et al., Melt processing for obtaining  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$  superconductors with high  $T_c$  and large  $J_c$ . J. Appl. Phys. Lett, 1994,65:633-635
- [6] Hu A. M., Zhao Z. X., Wende C., et al. Superconducting properties of melt-textured  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$  prepared in air. J. Physica C, 1997,278 :43-48
- [7] Si P. Z., Fan Z. G., Xu C. W.. Behavior of  $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$  in the zone-melted  $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$  [J]. Journal of the Chinese Rare Earth Society, 2000, 18 (Proceedings of Physico-chemistry of Metallurgy) : 311-314
- [8] Liang J. K., Che G. C., Chen X. L.. Phase relation and crystal structure in the system of high  $T_c$  oxide superconductors [M].Beijing : Science Press, 1994. 197