Partial Melting in Filamentary NSG123 Superconductors under Various Oxygen Atmospheres

著者	渡辺　和雄
journal or publication title	IEEE Transactions on Applied Superconductivity
volume	18
number	2
page range	1204-1207
year	2008
URL	http://hdl.handle.net/10097/47192

doi: 10.1109/TASC.2008.921213

Partial Melting in Filamentary NSG123 Superconductors Under Various Oxygen Atmospheres

Yumiko Ikebe, Eriko Ban, Yoshiharu Matsuoka, Gen Nishijima, and Kazuo Watanabe

***Abstract*—Precursor filaments with starting composition $(Nd_{0.33}, Sm_{0.33}, Gd_{0.33})$: Ba : Cu = 1.18 : 2.12 : 3.09 were prepared by a solution spinning method. Samples were partially melted at temperature range of 1020–1090°C in flowing $0.1\%O_2$ + Ar, $1\%O_2$ + Ar and $20\%O_2$ + Ar and then oxygenated in pure $100\%O_2$ gas. The T_c value decreased from 91.3 K to 88.8 K with increasing oxygen concentration in atmosphere gas. A transport J_c value higher than 10^4 A/cm^2 at 77 K and 0 T was showed over a wide temperature range of 1030–1080°C in $0.1\%O_2$ + Ar and 1040–1090°C in $1\%O_2$ + Ar. Especially, the $0.1\%O_2$ + Ar sample partially melted at 1050°C and the $1\%O_2$ + Ar sample at 1060°C exhibited the highest J_c value of 2.7×10^4 A/cm^2 and 2.5×10^4 A/cm^2, respectively. The transport J_c value of the sample melted in flowing $0.1\%O_2$ + Ar was maintained higher than 2.4×10^3 A/cm^2 at 77 K in applied magnetic fields up to 17 T. On the other hand, the maximum J_c value at 77 K and 0 T for the sample treated in $20\%O_2$ + Ar melted at 1080°C showed 5.4×10^3 A/cm^2 at most, and the superconductivity was disappeared at magnetic field of 7 T.**

***Index Terms*—Critical current density, filamentary NSG123 superconductors, magnetic field behavior.**

I. Introduction

IT IS well known that the bulk $LREBa_2Cu_3Oy$ (LRE: Light Rare Earth = Nd, Sm, Eu, Gd; LRE123) superconductors with $LRE_{1+x}Ba_{2-x}Cu_3Oy$ solid solution (LRE123ss) show high critical temperature (T_c) and good superconductivity in magnetic fields. Some studies employing oxygen controlled melt growth (OCMG) have reported that the amount of LRE123ss in LRE123 superconductor is controlled through the control of oxygen partial pressure during melt process [1]–[3]. Actually, Eu123 filament treated in oxygen reduced atmosphere of $0.1\%O_2$ + Ar exhibited the excellent critical current density (J_c) value of 9.6×10^3 A/cm^2 at 77 K and 10 T [4].

It is important to understand the flux dynamics for further J_c improvement over the entire field range. Among a number of approaches in order to enhance the J_c value in a high magnetic field, LRE123 in which LRE site is consisted with two, three and four LRE elements has been examined. The ternary (Nd,Eu,Gd)-Ba-Cu-O (NEG123) bulk superconductor with excellent J_c behavior was reported that the respective LRE elements in this material contribute to pinning in different manners [5]. The role of three LRE elements has discussed in [5] that Nd mainly contributes flux pinning at low magnetic fields, Eu controls the second peak position and irreversibility field, and Gd slightly enhances intermediate and high field J_c value. Unlike bulk type LRE123 superconductors, however, there is little information on the properties for wire type ternary LRE123 superconductors.

The purpose of this study is to establish the preparation condition for filamentary (Nd,Sm,Gd)-Ba-Cu-O (NSG123) superconductors prepared by a solution spinning method and to examine the influence of oxygen partial pressure during melt processing on J_c. The field dependence of transport J_c at various temperatures from 77 K to 85 K for filamentary NSG123 superconductors optimally treated in a different oxygen concentration in flowing gases is also examined.

II. Experimental Procedure

The experimental procedure of filamentary NSG123 precursor was almost the same as published elsewhere [6]. A filamentary NSG123 precursor with starting composition of $(Nd_{0.33}, Sm_{0.33}, Gd_{0.33})$: Ba : Cu = 1.18 : 2.12 : 3.09 was fabricated by a solution spinning method, using a homogeneous aqueous solution containing mixed acetates of $Nd(CH_3COO)_3 \cdot H_2O$, $Sm(CH_3COO)_3 \cdot 4H_2O$, $Gd(CH_3COO)_3 \cdot 4H_2O$, $Ba(CH_3COO)_2$ and $Cu(CH_3COO)_2 \cdot H_2O$, poly (vinyl alcohol), propionic acid and 2-hydroxy isobutiric acid. The as-drawn filament was heated 450°C at a heating rate of 25°C/h, and then heated to 900°C for 15 min in flowing pure oxygen gas to remove volatile components and CO_2. The calcined samples were partially melted at temperature range of 1020–1090°C for 30 min in flowing gas with differential oxygen concentrations, $0.1\%O_2$ + Ar (sample A), $1\%O_2$ + Ar (sample B) and $20\%O_2$ + Ar (sample C). And then, samples were cooled in two-steps; first cooling step from partial melting temperature to 910°C was carried out at a cooling rate of 20°C/h and the second step from 910°C to 500°C at a cooling rate of 50°C/h. After partial-melting, oxygenation of the samples was processed by a two-step treatment.

The T_c and J_c at 77 K and 0 T were measured by a standard DC four-probe resistive method. Silver paint was used to connect the silver sputtered parts of the sample to Ag electrodes of 100 μm in diameter for supplying DC currents and Ag

Manuscript received August 27, 2007. This work was supported in part by the 21st Century COE Program of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Y. Ikebe, E. Ban, and Y. Matsuoka are with the Department of Materials Science and Engineering, Meijo University, Nagoya 468-8502, Japan (e-mail: m0641501@ccmailg.meijo-u.ac.jp).

G. Nishijima and K. Watanabe are with the High Field Laboratory for Superconducting Materials, IMR, Tohoku University, Sendai 980-8577, Japan.

Digital Object Identifier 10.1109/TASC.2008.921213

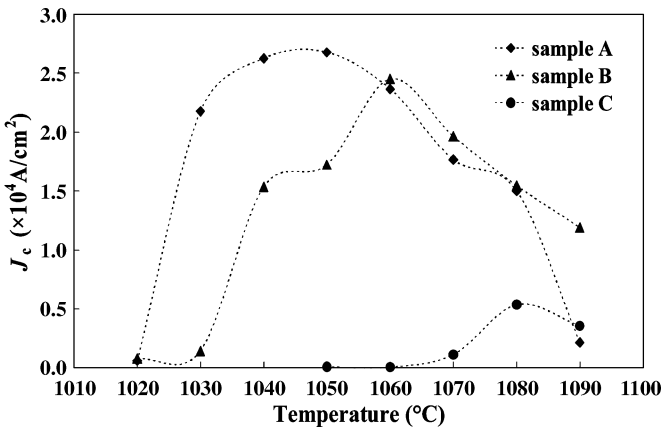

Fig. 1. The relationship between transport J_c and partial melting temperature at 77 K and self-field for filamentary NSG123 superconductors.

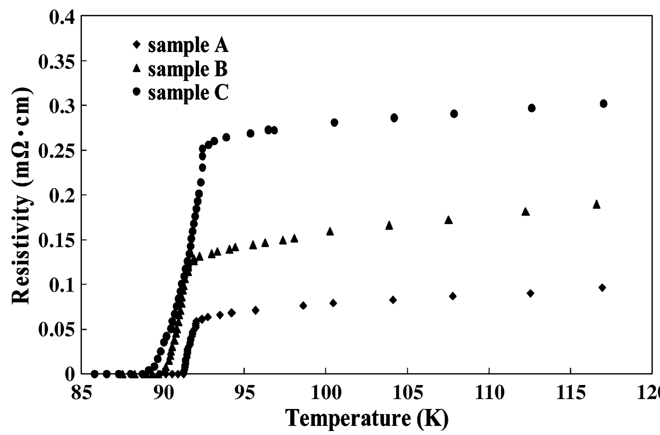

Fig. 2. Resistivity as a function of temperature for the filamentary samples.

electrodes of 75 μm in diameter for voltage leads. The sample was embedded on the substrate at the arbitrary direction for the sample diameter using epoxy resin and mounted on a critical-current-measuring holder. External magnetic fields were applied in direction perpendicular to filament length using a 20 T superconducting magnet at the High Field Laboratory for Superconducting Materials, Tohoku University. The pulse current was passed along the direction of the filament length and perpendicular to the applied magnetic field. The microstructure of the filaments was also studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray (EDX). In addition, the decomposition temperature of the NSG123 filaments was examined using the differential temperature analysis (DTA).

III. Results and Discussion

The diameter of the filaments after melt processing were about 80–120 μm. The dense texture and a little void were observed for each sample. A number of $(Nd, Sm, Gd)_2BaCuO_5$ (NSG211) particles of diameter 1–3 μm were dispersed in NSG123 matrix for samples A and B. On the contrary, a little NSG211 particle less than 1 μm in diameter were dispersed for sample C.

Initially, we examined the effects of partial melting temperature on the superconductivity. Fig. 1 shows the relationship between transport J_c at 77 K, 0 T and partial melting temperature of filamentary NSG123 superconductors. Samples were partially melted in gas with three different oxygen concentrations. Both samples A and B treated in low oxygen concentration show high J_c value compared with that of sample C melted in $20\%O_2 + Ar$ gas. In the case of samples A and B, the J_c value higher than 10^4 A/cm^2 are obtained over a wide temperature range of 1030–1080°C and 1040–1090°C, respectively. Sample A treated at 1050°C and sample B melted at 1060°C attained the highest J_c value of 2.7×10^4 A/cm^2 and 2.5×10^4 A/cm^2, respectively. On the contrary, sample C prepared using present condition exhibit rather low J_c value of 5.4×10^3 A/cm^2 at most. It was found that the J_c of filamentary NSG123 superconductors are strongly influenced by the oxygen concentration in atmosphere gas and partial melting temperature. The optimum melting temperature of each samples increases with increasing oxygen concentration in atmosphere.

The decomposition temperature of NSG123 filament was also examined in precisely controlled oxygen concentration in Ar gas. From our DTA results, the decomposition temperature of samples A, B and C were 1020°C, 1028°C and 1065°C, respectively. It is known that the decomposition temperature increased with increasing oxygen concentration [7]. It was reported the bulk type LRE123 superconductors with three different LRE elements melted at 40°C higher than the decomposition temperature showed high J_c value [7]. It should be noted that the relationship between the optimum partial melting temperature and the decomposition temperature of present sample showed the similar tendency to another report.

Fig. 2 shows the relationship between the temperature and resistivity of each sample melted at optimum partial melting temperature; sample A-1050°C, sample B-1060°C and sample C-1080°C. All samples show metallic behavior from room temperature to transition onset about 92 K, and then resistivity rapidly decreases to zero. The T_c value of the samples A, B and C exhibited 91.3 K, 89.7 K and 88.8 K, respectively. It is clear that T_c value decreases and transition width increases with increasing oxygen concentration. It is well known that the T_c value decreased with increasing x value of LRE123ss in LRE123 superconductors [8]. For sample C, x value of LRE123ss would increased due to melting in high oxygen concentration of $20\%O_2 + Ar$. Therefore, sample C showed the low T_c value of 88.8 K with a broad superconducting transition compared with those of samples A and B.

Fig. 3 shows XRD patterns for each samples partially melted at optimum temperature. The peaks corresponding to NSG123 and second phase NSG211 are observed. Sample A shows the pronounced splitting of peak around $2\theta = 32.5°$ and 32.8° corresponding to orthorhombic NSG123. However, the sprit was obscured with increasing oxygen concentration due to the $2\theta = 32.5°$ peak decreased with increasing oxygen concentration, the sprit of sample C disappeared. From experimental result of Fig. 2, we are considering that sample C is having NSG123ss of large x value. In this case, the orthorhombic NSG123 might be formed difficult through the lattice distortion by the replacement of LRE^{3+} ion on the Ba^{2+} site, therefore, the sprit of sample

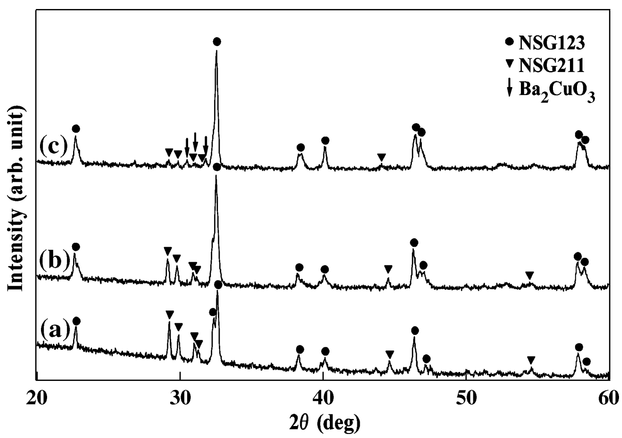

Fig. 3. X-ray diffraction patterns for sample A-1050°C (a), sample B-1060°C (b) and sample C-1080°C (c).

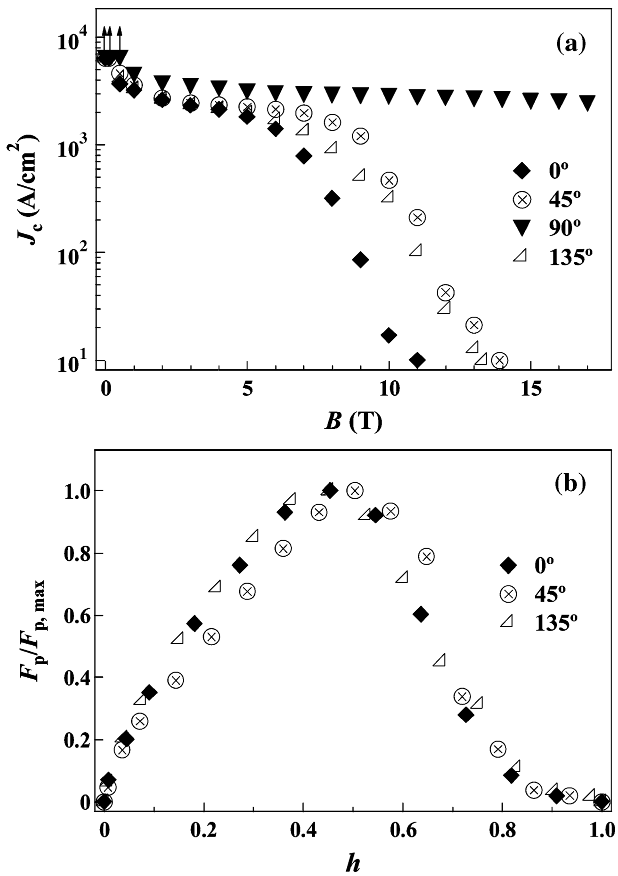

Fig. 4. Field dependence of transport J_c for sample A rotated at various angles between 0° and 135° (a). Volume flax pinning force $F_p/F_{p,max}$ as a function of reduced field $h = H_a/H_{irr}$ for sample A (b).

C disappeared. It should be also noted that reflection peak of NSG211 for sample C are reduced compared with that of the samples A and B. It seems that the peritectic reaction where the NSG211 dissolves in liquid and reacts with liquid is advanced due to as a result of used relatively slow cooling rate and in rich oxygen atmosphere. The reflection peak of Ba_2CuO_3 was also observed for sample C. This would be caused by relative Ba-rich composition phase generated in liquid phase at solidification for a large number of LRE elements substituted on Ba site compared with that of samples A and B, as a result, the Ba_2CuO_3 occurred in sample C was observed from XRD.

The field dependence of transport J_c for sample A were investigated in an applied magnetic field is shown in Fig. 4(a). We measured the J_c value of filamentary samples at 77 K in the magnetic field up to 17 T. The sample holder was rotated along the filament diameter at the angle ranging from 0° to 135°. Here, 0° was defined such that external magnetic fields were applied in direction parallel to the substrate surface where the sample was embedded. It is probable that applying a current of more than 0.3 A burn out the probe cable and it is break out the heat between the sample and current lead. Therefore, the arrows in this figure are standing for the J_c value when current of 0.3 A is applied, because the current J_c value is not measured. The J_c value of sample A rotated 90° gradually decreases with increasing applied fields up to 6 T. The J_c values are showed almost invariable values from 6 T to 17 T. It should be noted that the transport J_c value higher than 2.4×10^3 A/cm^2 could be maintained by applied magnetic fields up to 17 T. On the other hand, the sample rotated 0°, 45° and 135° as well as the 90° rotated sample gradually decreases with increasing applied magnetic fields around up to 6 T, but the J_c value drastically decreases with increasing applied magnetic fields over around 6 T, the superconductivity of 0°, 45° and 135° samples disappear around 11 T, 14 T and 13 T, respectively. This must be caused by the effective pinning of the sample A rotated 90° contribution such as intrinsic flax pinning and field induced pinning similar to the case of filamentary Eu123 superconductors [4]. Furthermore, Muralidhar *et al.* have reported that periodic nanometer-scale lamellas which higher and lower of NEG/Ba ratio regularly vary within twins appear in $(Nd_{0.33}, Eu_{0.38}, Gd_{0.28})Ba_2Cu_3Oy$ bulk superconductors with 3–7 mol%$(Nd_{0.33}, Eu_{0.33}, Gd_{0.33})_2BaCuO_5$ melted in $0.1\%O_2 + Ar$, these samples show high irreversibility field of about 14 T at 77 K and $B//c$ [9]. The nanometer-scale lamellas might exist in our sample A as well as the bulk type NEG123 superconductors with 3–7 mol% NEG211 of above report.

Useful data on the pinning mechanism can be obtained from the scaling analysis, Fig. 4(b) shows normalized pinning force density $F_p/F_{p,max}$ $(F_p = J_c \times H_a)$ as a function of reduced field $h = H_a/H_{irr}$ for sample A. Where, H_a is the applied magnetic field and H_{irr} is the irreversibility field which is obtained from $J_c - B$ curves using the criterion 10 A/cm^2. The scaling curve of the 90° sample is not represented, due to the irreversibility field exhibited over 17 T. The peak position of 0°, 45° and 135° samples show around $h = 0.45$, 0.50 and 0.45, respectively. These peak positions close to $h = 0.50$, suggested that the dominant pinning exhibited $\Delta\kappa$ pinning [10]. In spite of sample A treated in relatively low oxygen concentration in atmosphere, dominant pinning of sample A shows $\Delta\kappa$ pinning, this result might be caused by sample A was cooled by relatively slow cooling rate [6].

Fig. 5(a) shows field dependence of transport J_c at four kinds of temperature, 77, 80, 83 and 85 K for filamentary sample C of angle 0°. The J_c value drastically decreases to less than 1.3×10^3 A/cm^2 by applying only a magnetic field of 0.1 T due to the indicating week-link behavior at grain boundaries. And then,

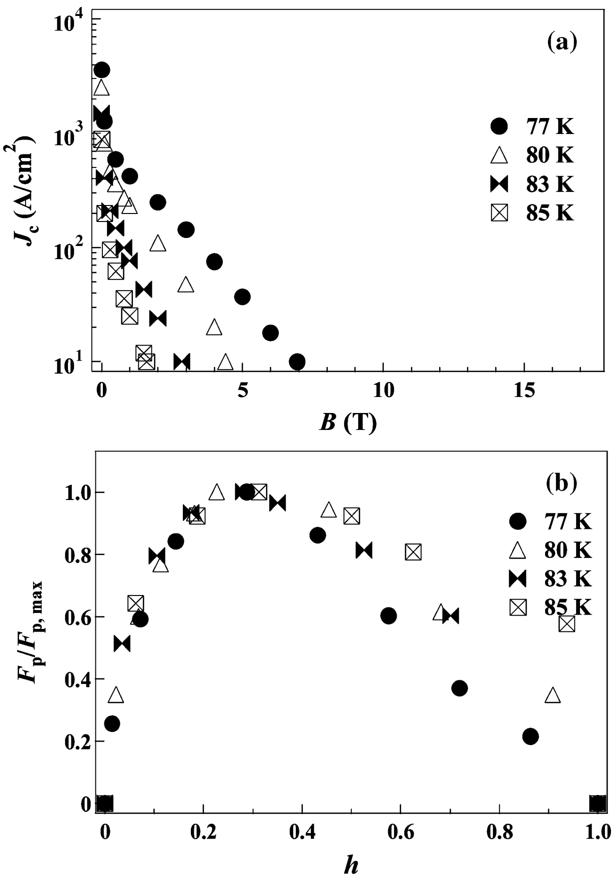

Fig. 5. The field dependence of transport J_c at four kinds of temperature for sample C (a) and volume pinning force as a function of reduced field is shown in (b).

the J_c value abruptly decreases with continuously increasing applied magnetic field, the irreversibility field at 77 K is shown about 7 T. It appears that the field dependence of J_c deteriorated for sample C compared with that of sample A. This result should be explained that the decreasing of NSG211 phase which is the effective pinning and the magnetic flux were off the angle of perpendicular to the c-axis.

Normalized pinning force density $F_p/F_{p,\max}$ as a function of reduced field $h = H_a/H_{irr}$ for sample C are also shown in Fig. 5(b).

The peak position of all temperature located at around $h = 0.3$, which corresponds to a normal-point pining according to the classical theory [10]. This result could be suggested that NSG123ss cluster with large x value in sample C transform to normal cluster at even self-field, hence, the peak of the scaling curve for sample C was located at $h \approx 0.3$. Besides, the Ba_2CuO_3 phases in sample C was measured from XRD, it should be considered that also a Ba_2CuO_3 phase was one of the effective normal pinning.

IV. Conclusion

We studied the fabrication and characterization of filamentary (Nd,Sm,Gd)-Ba-Cu-O superconductors prepared by a solution spinning method. Precursor filaments were partially melted in flowing $0.1\%O_2$ + Ar (sample A), $1\%O_2$ + Ar (sample B) and $20\%O_2$ + Ar (sample C) and then oxygenated in pure 100 $\%O_2$ gas. The critical temperature systematically decreased from 91.3 K (sample A) to 88.8 K (sample C) with increasing oxygen concentration in flowing gas. Sample A partially melted at 1050°C and sample B melted at 1060°C showed the highest J_c value of 2.7×10^4 A/cm^2 and 2.5×10^4 A/cm^2 at 77 K and 0 T, respectively. The transport J_c value higher than 2.4×10^3 A/cm^2 at 77 K of sample A rotated the optimized angle was able to maintain by applied magnetic fields up to 17 T. On the other hand, the maximum J_c value of sample C treated at 1080°C showed $J_c = 5.4 \times 10^3$ A/cm^2 at most. The superconductivity of sample C was disappeared at about 7 T. It was found that the superconductivity of NSG123 superconductors was strongly influenced by the oxygen concentration in atmosphere gas.

Acknowledgment

This work was performed at the High Field Laboratory for superconducting Materials, Institute for Materials Research, Tohoku University.

References

[1] S. I. Yoo, N. Sakai, H. Takaichi, and M. Murakami, "Melt processing for obtaining $NdBa_2Cu_3O_y$ superconductors with high T_c and large J_c," *Appl. Phys. Lett.*, vol. 65, pp. 633–635, 1994.

[2] H. Wu, K. W. Dennis, M. J. Kramer, and R. W. Mccallum, "Solubility limits of $LRE_{1+x}Ba_{2-x}Cu_3O_{y+\delta}$," *IEEE Appl. Supercond.*, vol. 6, pp. 87–107, 1998.

[3] N. H. Bubu, D. A. Cardwell, W. Lo, and A. M. Campbell, "Flux pinning in large $NdBa_2Cu_3O_{7-\delta}$ grains fabricated by seed-melt growth," *Phys. Rev. B*, vol. 61, pp. 735–740, 2000.

[4] E. Ban, T. Goto, K. Watanabe, and Y. Matsuoka, "Field dependence of J_c for filamentary Eu123 superconductors," *Jpn. J. Appl. Phys.*, vol. 41, pp. L1055–L1058, 2002.

[5] M. Muralidhar, M. Jirsa, N. Sakai, and M. Murakami, "Matrix chemical ratio and its optimization for highest flux pinning in ternary (Nd-Eu-Gd)$Ba_2Cu_3O_y$," *Supercond. Sci. Technol.*, vol. 15, pp. 688–693, 2002.

[6] Y. Ikebe, E. Ban, Y. Matsuoka, G. Nishijima, and K. Watanabe, "Critical current density of filamentary NSG123 superconductors in high magnetic field," *Physica C*, vol. 463–465, pp. 559–563, 2007.

[7] M. Muralidhar, H. S. Chauhan, T. Saitoh, K. Kamada, K. Segawa, and M. Murakami, "Effect of mixing three rare-earth elements on the superconducting properties of $REBa_2Cu_3O_y$," *Supercond. Sci. Technol.*, vol. 10, pp. 663–670, 1997.

[8] M. Murakami, "Key issues for the characterization of RE-Ba-Cu-O systems (RE: Nd, Sm, Eu, Gd)," *IEEE Appl. Supercond.*, vol. 6, pp. 51–59, 1998.

[9] M. Muralidhar, N. Sakai, N. Chikumoto, M. Jirsa, T. Machi, M. Nishiyama, Y. Wu, and M. Murakami, "New type of vortex pinning structure effective at very high magnetic fields," *Phys. Rev. Lett.*, vol. 89, pp. 237001-1–237001-4, 2002.

[10] D. Dew-Hughes, "Flux pinning mechanisms in type 2 superconductors," *Philos. Mag.*, vol. 30, pp. 293–305, 1974.