Effects of Gd$_2$BaCuO$_5$ addition on critical current characteristics in melt-processed (Nd, Eu, Gd)–Ba–Cu–O

M. Muralidhar *, M. Murakami

Superconducting Research Laboratory (SRL), ISTEC, 1-16-25, Shibaura, Minato-ku, Tokyo 105, Japan

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Abstract

We have investigated the effects of Gd$_2$BaCuO$_5$ (Gd211) addition on the microstructure and $J_c$–$B$ properties of oxygen-controlled-melt-growth (OCMG)-processed (Nd, Eu, Gd)–Ba–Cu–O system with scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and magnetization measurements. Compositional analyses revealed that small RE$_2$BaCuO$_6$ (RE211; RE: rare earth elements) particles consist mainly of Gd in the RE site, while large RE211 particles contain Nd, Eu and Gd despite the fact that only Gd211 was added to the system. Both zero field and peak $J_c$ increased with increasing Gd211 content; however, $J_c$ values were decreased when the amount of Gd211 reached 40 mol%. The sample (Nd, Eu, Gd)Ba$_2$Cu$_2$O$_y$ added with 30 mol% of second phase Gd211 showed respective critical current densities of 71 000 and 52 000 A/cm$^2$ in 0 T and 2.6 T at 77 K for fields parallel to the c-axis. These results indicate that Gd211 addition to (Nd, Eu, Gd)–Ba–Cu–O is effective in improving $J_c$ values through fine dispersion of Gd211.

Keywords: Melt processing; (Nd, Eu, Gd)123; Gd211; Pt addition; Microstructure; Critical current density

1. Introduction

The RE–Ba–Cu–O (RE: Nd, Sm, Eu, Gd) bulk superconductors prepared by the oxygen-controlled-melt-growth (OCMG) process [1] have a significant potential for high field engineering applications since they exhibit large critical current density ($J_c$) values even at 77 K. The OCMG process is melt processing in a reduced oxygen atmosphere, which enabled us to suppress the substitution of RE for Ba and thereby to achieve high $T_c$ in the RE–Ba–Cu–O system with a RE–Ba solid solution, which was first accomplished by Yoo et al. [1] and Murakami et al. [2] in the Nd123 system. In addition, it was found that the OCMG-processed RE–Ba–Cu–O exhibits superior flux pinning accompanied by a secondary peak effect in magnetization loops. Later, it was experimentally confirmed that such enhanced pinning is mainly due to the presence of RE-rich RE123 clusters about 10–50 nm in diameter [3]. Such clusters with depressed $T_c$ are superconducting in low fields. They are driven normal in high fields and thus can act as effective pinning centers, leading to the secondary peak effect [4–7].
It is also known that $J_c$ values of the Y–Ba–Cu–O can be improved by introducing fine Y211 inclusions [8,9]. Similarly, many groups [10–13] have observed $J_c$ enhancement with the addition of RE422/RE211 in the OCMG-processed RE–Ba–Cu–O, although $J_c$ values could be enhanced only in a low field region due to a relatively large average diameter of RE422/RE211. Therefore, the refinement of RE422/RE211 has been challenged by several groups through Pt and/or CeO$_2$ additions [14,15], some of which led to $J_c$ enhancement.

Recently, we have found that $J_c$ values of (Nd, Eu, Gd)–Ba–Cu–O composite could significantly be enhanced at 77 K mainly due to the fact that the size of RE211 could be reduced [16,17]. A critical current density ($J_c$) value of 60,000 A/cm$^2$ at 3 T and a large irreversibility field exceeding 7 T at 77 K for the fields parallel to the $c$-axis were achieved in the sample (Nd, Eu, Gd)–Ba–Cu–O with 40 mol% of (Nd, Eu, Gd)$_2$BaCuO$_4$ second phase particles. Transmission electron microscopic observation with compositional analyses confirmed that relatively large RE211 particles about 1 μm in diameter contain Nd, Eu and Gd, while small RE211 particles with an average diameter smaller than 0.1 μm mainly comprise Gd211 [17]. The mechanism that small Gd211 particles are formed in (Nd, Eu, Gd)–Ba–Cu–O system has not been yet clarified; however, the fact that small RE211 particles are mainly composed of Gd in the RE site suggests that it may be possible to achieve fine dispersion of 211 second phase particles simply by adding Gd211 instead of (Nd, Eu, Gd)211.

![Normalized Susceptibility vs Temperature](image1)

![Normalized Susceptibility vs Temperature](image2)

![Normalized Susceptibility vs Temperature](image3)

![Normalized Susceptibility vs Temperature](image4)

Fig. 1. Temperature dependence of normalized susceptibility for OCMG-processed (Nd, Eu, Gd)–Ba–Cu–O superconductors with different volume fractions of the Gd211 phase.
In the present paper, therefore, we studied the effect of Gd211 addition on flux pinning enhancement for the (Nd, Eu, Gd)–Ba–Cu–O system.

2. Experimental procedure

High purity Nd2O3, Eu2O3, Gd2O3, BaCO3 and CuO commercial powders (5 N) were weighed to have a nominal composition of (Nd, Eu, Gd)BaCuO3. The precursor powders were ground thoroughly and calcinated at 880°C for 24 h with intermediate grinding, and pressed into pellets, which were further sintered at 1020°C for 48 h.

Commercial high purity Gd211 powders were added to (Nd, Eu, Gd)123 with the volume fractions of 10%, 20%, 30% and 40 mol%. Pt was also added to all the samples, since Pt addition was effective in reducing the size of RE 211 [16,17]. The heat treatment profiles of the melt processes for (Nd, Eu, Gd)–Ba–Cu–O composites were scheduled on the basis of differential thermal analysis (DTA) results.

The mixed powders were first pressed into pellets 20 mm in diameter and 15 mm in thickness, which were then subjected to cold isostatic press (CIP) under a pressure of 2000 kg/cm². For melt growth, a MgO (100) seed was placed at the center top of the pellets which were then OCMG-processed in 0.1% partial pressure of O2 with a gas flow rate of about 300 ml/min. The details of the heat treatment schedules can be found elsewhere [18].

Fig. 2. Scanning electron micrographs of 211 second phase in OCMG-processed samples fabricated with Pt addition: (a) (Nd, Eu, Gd)–Ba–Cu–O + 10 mol% of Gd211; (b) (Nd, Eu, Gd)–Ba–Cu–O + 20 mol% of Gd211; (c) (Nd, Eu, Gd)–Ba–Cu–O + 30 mol% of Gd211; and (d) (Nd, Eu, Gd)–Ba–Cu–O + 40 mol% of Gd211.
For oxygen annealing, samples with dimensions of $1.5 \times 1.5 \times 0.5 \text{ mm}^3$ were cut from as-grown crystals and heat treated in flowing $O_2$ gas in the temperature range of $300$–$600^\circ\text{C}$.

Microstructural features of the samples were observed with an optical microscope and a scanning electron microscope (SEM). The size and volume fraction of the Gd211 second phase trapped in the Nd, Eu, Gd123 matrix were determined with SEM micrographs using an image processing system.

The $T_c$ measurements were performed with a Quantum Design MPMS-7 superconducting quantum interference device (SQUID) magnetometer with an applied magnetic field of 10 Oe. Magnetization loops were measured at 77 K using a 7 T superconducting magnet with fields applied parallel to the $c$-axis. The $J_c$ values were calculated based on the extended Bean critical state model from the following equation:

$$J_c = \frac{20\Delta M}{[a(1 - a/(3b))]}.$$

where $J_c$ is in A/cm$^2$, $\Delta M$ is the magnetization hysteresis during the increasing and decreasing field processes in emu/cm$^3$, $a$ and $b$ $(a < b)$ in cm are the cross-sectional sample dimensions perpendicular to the applied magnetic field.

### 3. Results and discussion

#### 3.1. Effect of Gd211 addition on $T_c$

Fig. 1 shows the temperature dependence of direct current (DC) magnetic susceptibility for (Nd, Eu, Gd)–Ba–Cu–O samples with different amounts of Gd211. The onset $T_c$ of the sample with 10 mol% Gd211 was 93.1 K with a transition width less than 1 K, while for the samples with 20 to 40 mol% Gd211 second phase, the onset $T_c$ was somewhat lower. Such a slight depression of $T_c$ with increasing RE211 content has also been observed in other OCMG-processed RE–Ba–Cu–O [16], which may be attributed to the fact that the presence of excess Gd211 during the melt growth stage will shift the matrix composition toward RE rich direction, thus leading to a slight depression of $T_c$.

#### 3.2. Microstructural observations

Fig. 2a–d shows the SEM micrographs of polished surfaces for (Nd, Eu, Gd)–Ba–Cu–O samples with 10–40 mol% Gd211 second phase. It is clear that RE211 particles are finely dispersed in the RE123 matrix like the case of (Nd, Eu, Gd)123/(Nd, Eu, Gd)211 composite [17,19], showing that an addition of Gd211 alone instead of (Nd, Eu, Gd)211 is also effective in achieving fine dispersion of the second phases.

Table 1 summarizes the results of chemical compositional analyses for the sample with 30 mol% of Gd-211. The RE123 matrix has a relatively uniform composition with the chemical ratio of Nd:Eu:Gd close to 2:2:5, which shows that Gd elements are supplied from Gd211 to the RE123 phase during the peritectic reaction. It is also notable that there are two types of RE211 with different sizes in that large particles contain Nd, Eu and Gd while small particles mainly consist of Gd in the RE site. We can suppose that large RE211 particles are produced by the peritectic decomposition of RE123 phase since only Gd211 was added as the starting powders. Here, the fraction of Gd element in the RE site of RE211 is larger than that of the RE123 matrix. Such a high fraction of Gd in the RE site may imply that large particles are grown from Gd211 which can act as nucleation centers. In the case of small RE211 particles, it is probable that Gd211 particles initially

<table>
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<th>S. number</th>
<th>Area</th>
<th>Nd</th>
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<th>Gd</th>
<th>Ba</th>
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<td>0.844</td>
<td>1</td>
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<tr>
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<td>SP (big2)</td>
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<td>0.241</td>
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<td>SP (big3)</td>
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added to the system are retained, which may be supported by the fact that the amount of Nd and Eu elements is negligibly small in small RE211 particles. However, we should note the fact that in (Nd, Eu, Gd)123/(Nd, Eu, Gd)211 composites, small Gd211 particles can also be dispersed even though added RE211 particles are (Nd, Eu, Gd)211, which implies that Gd211 is formed on the way of cooling. In process, RE123 is formed from the following peritectic reaction:

$$\text{RE}_2\text{BaCuO}_5 + \text{L}(3\text{BaO} + 5\text{CuO}) = 2\text{REBa}_2\text{Cu}_3\text{O}_y.$$  

Here, it is important to note that unlike the normal peritectic reaction, once RE123 crystal is formed, RE211 does not function as a nucleation site for RE123 and instead decomposes to form RE-rich solution at the growth front of RE123, which then provides the driving force for further growth of RE123 crystal. Since the equilibrium solute content is higher for Nd and Eu than Gd, even when the RE211 contains Nd, Eu, and Gd, it has a chance to preferentially deliver Nd and Eu, leading to the formation of Gd211 particles.

### 3.3. Effect of Gd211 addition on flux pinning

Fig. 3 shows field dependence of $J_c$ for the (Nd, Eu, Gd)–Ba–Cu–O samples with different amounts of Gd211 measured at 77 K for fields applied parallel to the $c$-axis. All the samples exhibit relatively high irreversibility fields accompanied by the secondary peak effect at 2.5 to 3 T. Here, it is interesting to note that, for the samples with 10 and 20 mol% Gd211, the irreversibility fields ($77 \, \text{K, } H||c$)

![Graphs showing $J_c-B$ properties](image)

Fig. 3. $J_c-B$ properties (77 K, $H||c$-axis) for (Nd–Eu–Gd)–Ba–Cu–O superconductors with different volume fractions of the Gd 211 phase. All the samples are prepared by Ar—0.1% partial pressure of O$_2$. 

exceed 7 T, while those fields are below 7 T for the samples with 30 and 40 mol% Gd211, although $J_c$ is higher in low and intermediate fields. As presented in Fig. 1, an addition of Gd211 caused a depression of $T_c$, which probably led to the deterioration of the irreversibility field. The fact that $J_c$ decreases when the Gd211 content is increased from 30 to 40 mol% is also ascribable to a depression of $T_c$ value.

4. Summary

Melt-textured (Nd, Eu, Gd)–Ba–Cu–O samples with different concentration of Gd211 second phase were prepared by the OCMG process. Microstructural observations demonstrate that fine dispersion of RE211 is possible even when we added Gd211 second phase to the (Nd, Eu, Gd)123 system, which lead to high $J_c$ values. For the sample with 30 mol% Gd211, a large critical current density ($J_c$) of 71 000 and 52 000 A/cm² were achieved at 77 K 0 T and 2.6 T, respectively, for $H||c$-axis.

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References