High flux pinning in ternary (Nd–Eu–Gd)Ba$_2$Cu$_3$O$_y$ superconductors at 77 K

M. Muralidhar *, M. Jirsa 1, N. Sakai, M. Murakami
Superconductivity Research Laboratory (SRL), ISTEC, Division 3, 1-16-25 Iioka-Shibaura, Minato-ku, Tokyo 105-0023, Japan
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Abstract
The optimisation of ternary (Nd–Eu–Gd)Ba$_2$Cu$_3$O$_y$ (NEG) bulk quasi-crystals has been carried out to achieve high pinning at 77 K. For this purpose we prepared samples with various Nd:Eu:Gd ratios in the NEG compound. Our experimental results suggest that a suitable combination of the three elements on the rare earth site can enhance flux pinning at low, intermediate, and high magnetic fields. This is thus an effective tool for tailoring properties of this material according to requirements of the particular application. We show that the maximum flux pinning can be achieved in the whole magnetic field range (at 77 K) when very fine (sub-micron) secondary phase particles are dispersed in a superconducting 123 matrix with an optimum Nd:Eu:Gd ratio.

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1. Introduction
Because of the high critical current densities and high irreversibility field at 77 K achieved in melt-textured (LRE)Ba$_2$Cu$_3$O$_y$ (LRE: Nd, Sm, Eu, Gd) superconductors, these compounds are of a great importance for high-field power applications such as superconducting magnetic bearings, flywheel energy storage systems, and bulk superconducting magnets [1–3]. Recent experiments have proved that among the RE-123 compounds the ternary (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ (NEG-123) bulk superconductors exhibit highest critical current density and irreversibility field, along with a uniform microstructure [4,5]. Typical for these materials is a strongly developed secondary peak providing a large $J_c$ at high magnetic fields. In some cases the peak $J_c$ almost reaches the required engineering values of order 100 kA cm$^{-2}$ at 77 K [6]. A further improvement is still needed to satisfy the margin for safe operation at 77 K targeted for engineering applications.

In the present work we studied the change of structural modulation in NEG-123 matrix caused by variation of Eu/Gd and Eu/Nd ratio affects and
its effect on magnetic properties. In the first set of the samples we fixed the amount of Nd and changed the ratio of Eu and Gd. In the second set, the amount of Gd was kept constant and the Eu/Nd ratio was varied.

2. Experimental conditions

In the first step, high-purity commercial powders of Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$ and CuO were mixed in nominal compositions of (Nd$_{0.33}$, Eu$_{0.66-x}$, Gd$_x$)Ba$_2$Cu$_3$O$_y$ and (Nd$_x$, Eu$_{0.66-x}$, Gd$_{0.33}$)-Ba$_2$Cu$_3$O$_y$ where $x$ ranged from 0 to 0.33. The starting powders were thoroughly ground and calcined at 880 °C for 24 h with intermediate grinding, then pressed into pellets. Sintering was carried out at 900 °C for 15 h. This process was repeated three times under the oxygen partial pressure ($p_{O_2}$) of 0.1% O$_2$. In the second step, calcined powders were pressed into pellets of 20 mm diameter and 15 mm thickness using cold isostatic pressing of 200 MPa.

The peritectic decomposition temperature determined with differential thermal analysis measurements was used to schedule the heat treatment profile of the OCMG process for different NEG samples. Finally, a MgO(100) seed was placed at the centre of the top surface of the pellet, which was subsequently OCMG-processed in 0.1% $p_{O_2}$ atmosphere. In the OCMG-process the samples were heated to $T_1$ ($T_p + 90$ °C) in 4 h and held 30 min, cooled to $T_2$ ($T_p + 3$ °C) in 30 min, and then cooled by 50 °C with a cooling rate of 0.5 °C/h and subsequently 50 °C with a cooling rate of 1 °C/h followed by furnace cooling.

For oxygenation, small specimens with dimensions of $a \times b \times c = 1.5 \times 1.5 \times 0.5$ mm$^3$ were cut from the as-grown crystals and annealed in flowing O$_2$ gas as follows. The samples were heated to 600 °C at the rate 300 °C/h, held at 600 °C for 1 h, cooled to 500 °C at the rate of 8 °C/h, cooled to 400 °C at the rate 4 °C/h, then cooled to 300 °C at the rate 2 °C/h, held there for 150 h, and finally left in the furnace to cool down to room temperature.

Magnetization hysteresis loops in fields from $-2$ to $+7$ T were measured at 77 K using a commercial SQUID magnetometer (Quantum Design, model MPMS7). To minimize field inhomogeneity, the scan length was restricted to 1 cm. The external magnetic field was applied parallel to the c-axis of the samples. The magnetic $J_c$ values were estimated based on the extended Bean’s critical state model using the relation:

$$J_c = \frac{2\Delta m}{a^2d(b - a/3)}$$

where $d$ is the sample thickness and $a$, $b$ are cross sectional dimensions, $b \geq a$ [7].

3. Experimental results

Fig. 1 shows the field dependence of $J_c$ for NEG-123 samples with various Nd/Eu ratios measured at 77 K for fields parallel to the c-axis. In all the samples the Gd content was kept constant and the Nd/Eu ratio was varied. A clear secondary peak was observed in all the samples. As $x$ in (Nd$_{0.66-x}$, Eu$_x$, Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ decreased from 0.33 to 0.0 (Fig. 1(a)), the secondary peak position moved from 3 to 1 T. At the same time the irreversibility field changed from 7 to 3 T. Evidently, an enrichment of Nd (accompanied by deficiency of Eu) causes a reduction of the irreversibility field leading also to the shift of the secondary peak to lower fields.

In the second system we varied the Nd/Eu ratio in reversed direction: changing $x$ in (Nd$_x$, Eu$_{0.66-x}$, Gd$_{0.33}$)-Ba$_2$Cu$_3$O$_y$ from 0.33 to 0. The field dependence of the critical current densities at 77 K are shown in Fig. 1(b). In contrast to the previous case, the irreversibility field (around 7 T) and the secondary peak position (around 3 T) were nearly independent of the chemical ratio. These results imply that an enrichment of Eu helps to keep the peak position and the irreversibility field high.

In order to verify the role of Eu in the NEG system, in the next series of samples the content of Nd was kept constant and the Eu/Gd ratio was varied in (Nd$_{0.33}$, Eu$_{0.66-x}$, Gd$_x$)-Ba$_2$Cu$_3$O$_y$ with $x$ changing from 0.33 to 0 (see Fig. 2). All the samples exhibited at 77 K the irreversibility field $B_{irr} \approx 7$ T and the secondary peak field $B_p = 3-3.5$ T. Only for the sample with Eu = 0.38 and 0.43 a slight enhancement of $B_{irr}$ (above 7 T) was
observed. It is in accord with the above result. Again an enrichment of Eu resulted in a high irreversibility field and consequently a high peak position. Our recent work on the \((\text{Nd}_{0.33},\text{Eu}_{x},\text{Gd}_{0.33})\)Ba\(_2\)Cu\(_4\)O\(_y\) system [8] showed that a decrease in Eu content \((x)\) led to a systematic decrease of the irreversibility field and the peak position.

The present study along with the former study [8] consistently show the importance of Eu for the enhancement of the irreversibility field and a high peak field at 77 K. On the other hand, a small deficiency of Nd or Gd did not appreciably affect the system performance. As reported in Ref. [8], Gd enrichment results in a strong enhancement of the peak \(J_c\) to nearly 100 kA cm\(^{-2}\). The growth of the peak height was accompanied by its narrowing and the shift to lower fields. Note that the narrowing and the shift of the peak to lower fields with increasing peak height was predicted by Kramer [9] for the shearing mechanism of vortex lattice movement among islands of strongly pinned vortices. According to this scenario the enrichment of Eu should correspond to a weaker point-like pinning, while the enrichment of Gd to a stronger point-like pinning. The only conclusion we can draw is that the variation of the chemical ratio in the NEG-123 matrix affects the high-field part of the \(J_c(H_a)\) curves in the way typical for a point-like disorder. We therefore believe that RE-123ss clusters are the dominant pinning centers in our samples.

Recently, we have found that the chemical ratio fluctuation on a microscopic scale in the NEG-123 samples depends on the matrix chemical compo-
The superconducting transitions measured by SQUID magnetometer were sharp and $T_c$ values were within 2 K, in both the samples, with increasing Eu/Gd and Eu/Nd ratio. The samples exhibit similar irreversibility fields and peak positions at 77 K with $H\parallel c$-axis. On the other hand, with the increase of Nd and Gd content at the expense of Eu the irreversibility field shifted from 7 T to lower magnetic fields. However, the origin of Eu effect on irreversibility field is not yet clear and further experiments are under way.

In the NEG-123 system the optimum matrix chemical ratio can be further combined with a proper secondary phase particles enhancing material performance at low fields. Fig. 3 shows the field dependence of $J_c$ at 77 K ($B\parallel c$) for the (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ system with 5 and 10 mol% of NEG-211. It is clear that low field critical current density and irreversibility field were dramatically improved with the addition of NEG-211. Therefore, an optimization of the matrix chemical ratio and the content of fine secondary phase particles in the NEG system assures a high critical current density in a broad field range.

4. Summary

The NEG-123 samples with different ratios of Nd:Eu:Gd were prepared by the OCMG-process. The magnetic measurements showed that Nd:Eu:Gd ratio in the NEG-123 matrix affects the pinning properties of this compound at intermediate and high fields, which can be used to tailor the pinning performance. A proper choice of the Nd:Eu:Gd ratio enables us to manipulate the secondary peak position in the range of 1–4 T at 77 K. High $J_c$ in a broad field range can be achieved by combining an optimum chemical ratio of Nd:Eu:Gd with an optimum concentration of sub-micron 211 particles.

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