Observation of record flux pinning in melt-textured NEG-123 superconductor doped by Nb, Mo, and Ti nanoparticles

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Flux pinning in melt-processed (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ “NEG-123” + 35 mol% Gd$_2$BaCuO$_5$ “NEG-211” (70 nm in size) composite doped by TiO$_3$, MoO$_3$ and Nb$_2$O$_5$ achieved record values. The optimum values of all three dopants were found to be around 0.1 mol\%. Transmission electron microscope (TEM) analysis found clouds of <10 nm sized particles in the NEG-123 matrix, shifting the pinning particle size distribution to significantly lower values. TEM by energy dispersive X-ray spectroscopy (EDX) analysis clarified that these nanoparticles contained a significant amount of Nb, Mo, and Ti. Appearance of nanometer-sized defects correlated with a significantly improved flux pinning at low and medium magnetic fields, which was particularly significant at high temperatures. In the Nb-doped sample, a record $J_c$ value of 925 kA/cm$^2$ at the secondary peak field (4.5 T) was achieved at 65 K, 640 kA/cm$^2$ at zero field at 77 K, and 100 kA/cm$^2$ at 90.2 K, the last value having been up to now considered as a good standard for REBa$_2$Cu$_3$O$_y$ “RE-123” materials at 77 K. The greatly improved $J_c$–$B$ performance in Nb/Mo/Ti doped samples can be easily translated to large-scale LRE-123 (LRE = light rare earths, Nd, Eu, Gd, Sm) blocks intended for real superconducting super-magnets applications.

1. Introduction

Melt-processed REBa$_2$Cu$_3$O$_y$ (RE-123) bulks possess a big potential for use in strong compact superconducting magnets [1]. Relatively small RE-123 pellets can trap magnetic fields by order of magnitude higher than the best hard ferromagnets [1,2]. One can expect that superconducting magnets will in a close future enter the market as the basic parts of compact magnetic resonance (NMR), drug delivery systems, water cleaning, wind power plants, medical diagnosis, and other applications [3,4]. In all these cases high critical currents and irreversibility field are the most important issues. The LRE-123 (LRE = light rare earths, Nd, Eu, Gd, Sm) compounds are characterized by far better electromagnetic properties than the others from the RE-123 family. This is because the LRE ions have a comparable size with Ba, can enter its positions in the 123 lattice and vice versa and form thus nanometer-scale solid solution clusters, an additional source of point-like pinning [5]. The role of such clusters is similar to that of oxygen-deficient zones in all RE-123 composites: they are responsible for formation of the secondary peak on the magnetization curve and on the related $J_c(B)$ dependence [6]. As all LRE ions form solid solution with barium, a strong pinning appears also in binary, ternary and quaternary LRE-123 compounds [7–9]. In these mixed materials one can also vary the LRE elemental ratio. Due to a slight difference in LRE ion sizes, the LRE ratio variation, especially in ternary and quaternary composites can affect the local tensions in the material matrix and in principle contribute to the pinning performance. Microstructure observations clarified that one can create nanoscale arrays in these materials and dramatically improve pinning at high magnetic fields [10]. The $H_{irr}$ values obtained in this way were at liquid nitrogen temperature twice to thrice those of single-elemental compounds, e.g. Nd-123 or Y-123 [2]. Besides, the melt-process technology enables introduction of non-superconducting secondary phase particles, RE$_2$BaCuO$_5$ (RE-211) that were found to enhance pinning at low magnetic fields. This increase is inversely proportional to a power of the size of such “large” particles (large with respect to the vortex core size, 2$\xi$). Although the secondary phase particles refinement up to the nanometer scale had been for a long time considered impossible, with the ZrO$_2$ ball milling of LRE-211 particles this goal was achieved. Such particles (in the size of 70–150 nm) not only survived the melt-texturing process but also further reduced their size up to 20–50 nm. Micro-chemical analysis identified these defects as
Zr-rich ZrBaCuO and (NEG, Zr) BaCuO ones [11]. The effect of Zr in the particles size diminution stacks obviously in the chemical inertia of Zr in the superconductor matrix. Creating nanoscale particles based on some other inert elements, like MgO [12] or Y2Ba4CuZrO7 [13] proved this hypothesis. Use of the initial powder composed of the nano-sized REBa2Cu3ZrOy particles and 35 mol% of sub-micron Gd-211 precipitates led to the super-current density around 270 kA/cm² at 77 K. This improvement extended up to liquid oxygen temperature. Our experience with the nanoscale Zr-rich particles [11] motivated us in testing the effect of doping by nanoparticles from the same chemical group, namely Ti, Mo, and Nb. And really, NEG-123 doped by 0.1 mol% of nanometer sized TiO3, MoO3 and Nb2O5 particles exhibited a further improvement in pinning performance. In this paper, emphasis is placed on the microstructure and chemical analysis of the nanoparticles of various sizes, and on magnetic properties estimated at various temperatures, especially around 77 K.

2. Experimental

High-purity commercial powders of Nd2O3, Eu2O3, Gd2O3, BaCuO2 and CuO were mixed in a nominal composition of (Nd0.33Eu0.33Gd0.33)Ba2Cu3Oy. The starting powders were thoroughly ground and calcined at 870 °C for 20 h and then pressed into pellets. Sintering was performed at 890 °C for 15 h. This process was repeated three times under controlled oxygen partial pressure (pO2) of Ar/1%pO2. In the second step, the powders of Gd2O3, BaO2, and CuO were mixed in the nominal composition of Gd2BaCuO5 and calcined three times at 840 °C, 870 °C and 900 °C for 10 h. The calcined Gd-211 powders were milled using Y2O3–2. Experimental atures, especially around 77 K.

Results and discussion

Fig. 1 shows the temperature dependence of dc magnetization in zero-field-cooled (ZFC) and field-cooled (FC) modes in magnetic field 1 mT for NEG-123 + 35 mol% Gd-211, 1 mol% CeO2 and 0.5 mol% Pt samples with 0.1 mol% of TiO3, MoO3, and Nd2O5. All the samples exhibited a similar sharp superconducting transition with ATc of about 1.5 K. As shown in the close-up near the transi-

tion temperature (the inset of Fig. 1), the onset Tc for all dopands is similar, about 93 K. This shows that the small quantity of any of the dopands does not negatively affect superconductivity of the samples.

The critical current density at 65 K, 77 K, 87 K, and 90 K of all the composites is presented in Fig. 2. In all samples the remnant critical current density dramatically increased in the whole range of temperature, from 65 K up to the boiling point of liquid oxygen (90.2 K). At 65 K the critical current density of TiO3 added sample reached more than 550 kA/cm² at 0 and 4.5 T and exceeded 450 kA/cm² over the whole range up to 5 T. Even better results were observed with MoO3 doping, when at 65 K super-currents reached more than 700 kA/cm² at 0 and 4.5 T and exceeded 610 kA/cm² over the whole range up to 5 T. The best pinning was, however, reached in the sample doped by Nb2O5, where the remnant JC at 65 K reached 925 kA/cm². At liquid nitrogen temperature (77 K) the remnant JC approached the record values of 320 kA/cm², 385 kA/cm², and 640 kA/cm² for Ti, Mo, and Nb additions, respectively, and JC at the secondary peak position, at 2 T, was 400 kA/cm² in the NbO2-doped sample. This result is by more than 50% better than the previous record values of NEG-123 and by...
more than order of magnitude better than in other RE-123 materials.

Boiling point of liquid argon (87 K) can represent another important temperature for applications. The remnant super-current densities of 150 kA/cm², 175 kA/cm², and 300 kA/cm² were recorded at this temperature for Ti, Mo, and Nb additions, respectively. The coolant closest to the critical temperature of most RE-123 is liquid oxygen (boiling point 90.2 K). The remnant super-current densities at 90.2 K reached 45 kA/cm², 60 kA/cm², and 100 kA/cm², respectively. All the $J_c$ values presented here are the highest reported so far for bulk RE-123 materials at the respective temperatures, coming close to the thin film limit. Therefore, the results might be important also for the technology of coated conductors. We note that the concentration of the dopands 0.1 mol% is the optimum and with further increase of Ti/Mo/Nb content the super-current density and irreversibility field again decrease [15].

![Figure 3](image1.png)

**Fig. 3.** Transmission electron micrograph of the NEG-123 sample with 0.1 mol% MoO$_3$ (left figure) and 0.1 mol% Nb$_2$O$_5$ (right figure). Note the formation of clouds of extremely small (<10 nm) (Nd, Eu, Gd)BaCuNbO particles in the NEG-123 matrix, which are obviously responsible for the highly improved flux pinning at the temperatures of 77 K and above, up to vicinity of $T_c$.

![Figure 4](image2.png)

**Fig. 4.** The EDX-HADDF-TEM pattern of 10 nm nanoparticles showing presence of Nb in the NEG-123 matrix (particles a1 and a2). On the other hand, the particle of 40 nm in size contains Zr, as in our earlier reports.
As a classification scheme for pinning performance the normalized volume pinning force density, $F_p/D_{pinmax}$, plotted against the reduced magnetic field $h = H/|H_{irr}|$ is sometimes used. The curves for the Ti/Mo/Nb-doped samples at 77 K and 87 K are shown in insets of Fig. 2. One can see that the $F_p(h)$ curves are nearly independent of the dopant type and the peak stands at the relatively high position, $h = 0.42$. According to the classical theory [17], this peak position would correspond to $\Delta T_p$ pinning. We note that this value is slightly lower than that observed in the earlier report [18]. This may be affected by the processing conditions and the amount of Gd-211. The main conclusion is that all dopands act in a similar way in the NEG-123 system.

To elucidate the origin of the critical current improvement, we observed the microstructure by TEM. Fig. 3 shows the typical TEM images of 0.1 mol% of Mo-added (left) and Nb-added (right) NEG-123 viewed from the (0 0 1) direction. In the images, three types of defects can be distinguished: large irregular inclusions of about 200–500 nm in size, round particles of 20–50 nm size, and clouds of spots less than 10 nm in diameter. The large quantity of the smallest particles was characteristic for these new NEG-123 materials. The EDX spectra of the nanoparticles in the Nb-doped sample are shown in Fig. 4. The analyzed spot of 2–3 nm in diameter enabled to unambiguously analyze even the smallest clusters. The quantitative analysis clarified that the large particles are Gd-211/Gd-rich-NEG-211, while the defects with size below 50 nm always contain a significant amount of Zr, in agreement with our earlier studies of the NEG-123 and SEG-123 systems [11,19]. EDX spectra showed that the small particles contained a significant amount of Nb (see Fig. 4; particle a1 and particle a2), while in the precipitates around 30–50 nm in size (particle a3) Zr was dominant, in correspondence with our previous report [19]. The exact chemical composition of the latter particles was determined as LREBa$_2$CuZrO$_6$. [19]. The appearance of such small defects correlates with the super-current enhancement in a wide temperature range, up to liquid oxygen temperature and the tendency in $J_c-H_a$ follows the theoretically predicted dependence for “large particle” [20,21]. It seems that these defects help to shift the “large” defect size distribution average to a lower value, resulting in critical current density enhancement at low and intermediate magnetic fields, without contributing to the random point-like defect disorder.

Although the size of the smallest particles came close to the vortex core size, $2\zeta_c$ (in YBCO $2\zeta_{ab} (77 K) \approx 4.5$ nm) and thus the limit of single-vortex interaction has been approached for these particles, no sign of a crossover to the secondary peak enhancement was observed. Note that a similar behavior was observed in the studies of Werner et al. [22] and Sauerzopf et al. [23,24] done on various RE-123 and Y-124 single crystals irradiated by fast neutrons. Might be that the crossover between multiple- and single-vortex pinning is rather sharp and we are still not close enough to it. Or, the present defects are in some sense different from the typical point-like defects (oxygen vacancies and/or the LRE-123 matrix chemical fluctuation [5,22,25].

4. Summary

We showed in this letter that doping of NEG-123 composites by 0.1 mol% of TiO$_3$, MoO$_3$, or Nb$_2$O$_5$ nanoparticles brought a significantly better electromagnetic performance. Transmission electron microscopy combined with energy dispersive X-ray spectroscopy analysis clarified that small nanoparticles dispersed in the material facilitated creation of Nb- or Mo-rich NEG-BaCuO nanoparticles with size less than 10 nm. As a result, a record $J_c$ value of 100 kA/cm$^2$ was achieved at 90 K and $J_c$ was high enough for levitation applications at this temperature. A record remnant critical current density of 925 kA/cm$^2$ at liquid nitrogen pumping up to 65 K was reached, illustrating the effectiveness and potentials of these materials for applications in a broad temperature range. Thus, the new NEG-123 composites are very promising for industrial super magnet applications with reasonably cheap cooling.

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