Irreversibility Field Above 14 T at 77 K in (Nd–Eu–Gd)Ba$_2$Cu$_3$O$_y$

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Abstract—In (Nd$_{0.33}$Eu$_{0.28}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$, a new type of nanometer-scale pinning center was created by choosing an appropriate matrix chemical ratio. Such a pinning center could be controlled via externally added small quantity of 211 (NEG-211 or Gd-211) secondary phase. Microstructure analysis combined with magnetic characterization clarified that the sample with a high irreversibility field always exhibits chemical modulation and formation of a special nanometer-scale lamellar structure. High magnification STM observations revealed that the nano-lamellae consist of rows of aligned NEG-rich clusters 3 to 4 nm in size. This new material with the Nd:Eu:Gd ratio of 1:1.25:0.65 combined with 5 mol% 211 secondary phase exhibits the high irreversibility peak position at around 4.5 T and the irreversibility field over 14 T at 77 K for $H_a \parallel c$-axis.

Index Terms—Critical current density, flux pinning, melt-processed bulk materials, STM.

I. INTRODUCTION

In YBa$_2$Cu$_3$O$_y$ (Y123), typical $B_{irr}$ values were in the range of 3–5 T for $B \parallel c$ at 77 K [1]. Neutron irradiation and heavy ion irradiation could dramatically increase pinning of this material, however the enhancement of $B_{irr}$ was small, which inevitably led to a rather pessimistic view for further dramatic enhancement of $B_{irr}$ values [2].

The first breakthrough came with Nd$_2$Ba$_2$Cu$_3$O$_y$ (Nd123), which exhibited higher $T_c$ and higher $B_{irr}$ than Y123 when they were melt-processed in low oxygen atmosphere [3]. The $B_{irr}$ value as high as 9 T at 77 K was achieved in this material. Microstructural observation showed that Nd rich Nd$_{1.97}$Ba$_2$Cu$_3$O$_y$ (Nd123ss) clusters are dispersed in Nd123 matrix, and they are believed to be responsible for the enhancement of $T_c$ and $B_{irr}$. The presence of such clusters was further confirmed with the presence of chemical fluctuation through compositional analyzes. Nd123 exhibited strongly developed secondary peak effect due to the field-induced pinning of Nd123ss clusters with depressed $T_c$ [4]. Later strong pinning with similar microstructure was confirmed in other RE123 (RE: Sm, Eu, Gd) materials that exhibit RE$_{1.12}$Ba$_2$Cu$_3$O$_y$ (RE123ss) type solid solution. In these RE123ss systems, an addition of secondary phase particles (RE211) was also effective in enhancing pinning, but again the irreversibility field was not improved. This is due to the fact that the $B_{irr}$ can only be raised by the introduction of defects that are active even in a high field region, and most pinning defects are not effective at high fields. In single crystalline Nd123 with high-pressure oxygen treatment, $B_{irr}$ of 12 T at 77 K ($B \parallel c$) has been achieved [5]. Although single crystals are not appropriate for practical applications, such results suggest that an enhancement of $B_{irr}$ may be possible for bulk materials even in practical dimensions.

The second breakthrough came with (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_y$ (NEG123) [6] in that the pinning performance could be tailored by controlling the chemical ratio of Nd, Eu, and Gd elements. For the NEG-123 system we prepared several batches of samples with various Nd:Eu:Gd ratios [7]. It was found that the optimization of the matrix chemical ratio together with an addition of small content of secondary phase particles result in a significant enhancement of irreversibility field. First, we believed that such an improvement is ascribed to the modification of chemical fluctuation in the matrix. Contrary to our expectation, the control of chemical ratio resulted in the creation of new type of pinning centers on nano-scale. Such new pinning centers led to a significant improvement of $B_{irr}$ to > 14 T at 77 K in this material, which paves a direct way for real high-field applications of high $T_c$ bulk materials.

II. EXPERIMENT

High-purity commercial powders of Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$ and CuO were mixed in quantities corresponding to a nominal composition of (Nd$_{0.33}$Eu$_{0.28}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$. 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 oxygen partial pressure (pO$_2$) of 0.1% O$_2$.

Next, commercial Nd-422, Eu-211, and Gd-211 powders were mixed in the ratio 1:1:1. Then, 0 to 40 mol% of NEG-211 were added to the NEG-123 powders. To further control the matrix chemical composition, in the next set we also added 0–10 mol% Gd-211 to the NEG-123 powders. 0.5 mol% of Pt was added for the secondary phase refinement, and also 10wt% of Ag$_2$O for improvement of the mechanical properties.

Finally, well-mixed [7] powders were pressed into pellets of 20 mm diameter and 15 mm thickness, which were consolidated by cold isostatic pressing with a pressure of 200 MPa. For differential thermal analysis (DTA) measurements, the powders were pre-treated at 925°C in flowing Ar-0.1% O$_2$ for 15 h. DTA measurements were performed under the same conditions to deter-
mine the peritectic decomposition temperature, $T_p$. This temperature was then used to schedule the heat treatment profile of the oxygen controlled melt growth (OCMG) process. All the samples were fabricated with the OCMG process, under oxygen partial pressure $0.1\%$ and gas flow rate of $300$ mL/min. The details of the heat treatment schedule can be found elsewhere [6].

For magnetic measurements small specimens with dimensions of $a \times b \times c = 2.04 \times 2.14 \times 0.48$ mm$^3$ were cut from as-grown pellets and annealed in flowing O$_2$ gas in a temperature range of $300-600$ °C [6]. The microstructure of these samples was studied with a transmission electron microscope (TEM), a dynamic force microscope (DFM), and a scanning tunnelling microscope (STM). Chemical composition of the matrix was analyzed by energy dispersive X-ray spectroscopy (EDX). Magnetization hysteresis loops ($M - H$ loops) were measured at $77$ K using a vibrating sample magnetometer (VSM) with the maximum field of $14$ T. 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 [8].

III. RESULTS AND DISCUSSION

A. Magnetization Characteristics

Fig. 1 shows the field dependence of the magnetization for (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_{y}$ sample with $0$ to $40$ mol% NEG-211 at $77$ K, for an applied field $H_a$ parallel to the c-axis. It is notable that with increasing NEG-211 content, the irreversibility field increases rapidly, reaching a maximum, then decreases. The irreversibility field exceeds $7$ T, and the secondary peak position lies at around $3.6$ T, when the initially added NEG-211 content is $<10$ mol%. With increasing NEG-211 content, the irreversibility field decreased to around $7$ T. The highest $B_{irr}$ was observed for the sample with $5$ mol% NEG-211. It is likely that externally added $211$ will change the matrix chemical composition during the melt-growth process [9]. Recent results on NEG-123 system with different chemical ratio clarified that matrix chemical composition is important parameter for improve the high field flux pinning at $77$ K [7].

In another series of experiment, we changed the NEG-211 secondary phase to Gd-211 and maintained the matrix chemical ratio the same as above (Fig. 2). In particular, we selected several samples with Gd-211 ranging from $0$ to $10$ mol%, to optimize the matrix composition by externally added $211$ content. Again, all six samples exhibited very high irreversibility fields at $77$ K for $H_a$ or c-axis (see in the Fig. 2). Most of the samples showed constant $M(H_a)$ performance up to $4$ T, which is very promising for high field applications. The irreversibility field increased with increasing the $211$ content, then decreased like the NEG-211. It should also be noticed that the $5$ mol% Gd-211 added samples re-produced a very high irreversibility field. Similar $M(H_a)$ properties were obtained for the samples cut from various locations in massive as-grown pellet, showing its good reproducibility. This led us to the conclusion that such high performance in pinning is not accidental but originates from the particular chemical ratio in NEG-123 matrix along with an appropriate amount of a secondary phase.

In order to evaluate the irreversibility field for NEG-123 sample with $5$ mol% NEG-211 at $77$ K (H || c-axis), we measured hysteresis loop using a vibrating sample magnetometer (VSM) with the maximum field of $14$ T and the field sweep rate of $0.6$ T/min. The critical current density ($J_c$) obtained from the Bean model is presented in Fig. 3, together with data of melt-processed Yb$_{2}$Cu$_3$O$_{y}$ and (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_y$ with a ratio of Nd:Eu:Gd = 1:1:1. Characteristically, the melt-processed YBCO sample does not exhibit the peak effect with the irreversibility field around $4$ T. OCMG processed NEG sample with the matrix ratio of 1:1:1 shows a clear secondary peak effect at $2$ T accompanied by a high irreversibility field around $7$ T. The most remarkable feature of the newly developed NEG sample (with a ratio of Nd:Eu:Gd = 1:1:2.5:0.85) is that the irreversibility field was over $14$ T (see inset of Fig. 3). A secondary peak was located at around $4.5$ T, and the $J_c$ value reached $70, 49,$ and $22$ kA/cm$^2$ at $4.5, 7,$ and $10$ T, respectively. The measurements at higher temperatures implies that the $B_{irr}$ is $15$ T at $77$ K [10]. This is the highest secondary peak posit
Fig. 3. Comparison of the field dependence of the critical current density (T = 77 K and H||c-axis) for melt-processed YBCO, OCMG processed (Nd0.33Eu0.33Gd0.33)Ba2Cu3Oy and newly developed (Nd0.33Eu0.33Gd0.33)Ba2Cu3Oy sample with 5 mol% NEG-211. Note the new NEG sample exhibits high critical current density (Jc) of 70 kA cm⁻² at the secondary peak around 4.5 T at 77 K (H||c). The inset shows that the irreversibility field exceeds 14 T.

Fig. 4. Transmission electron micrograph of (Nd0.33Eu0.33Gd0.33)Ba2Cu3Oy sample with 5 mol% NEG-211 viewed from a [001] direction. Note the modulation and nano-twinned-like structure observed inside the normal twins.

and the largest irreversibility field reported so far for RE-123 superconductors at this temperature.

8. Microstructure Analysis

To understand the magnetic performance, we observed the microstructure of (Nd0.33Eu0.33Gd0.33)Ba2Cu3Oy samples. Fig. 4 shows the dark-field TEM image of the sample with 5 mol% NEG-211 viewed from [1] direction. An important feature of this image is the modulation structure, and a structure of fine twin-like boundaries, inside the normal twins. These fine twin-like structure run over the normal twins with the spacing of few nano-meters. The formation of nano-twin-like structure in this sample could not be directly proved by the TEM analysis. We performed an additional study by means of dynamic force microscopy. Fig. 5 shows DFM image showing nanometer-scale lamellar in this sample and confirmed the modulation structure. We found similar images in different parts of samples. In any case, the matrix modulation and nanostructures exist in different parts of the pellet for the given matrix chemical ratio and NEG-211 concentration. We also found similar images in the samples with 3 and 7 mol% NEG-211. Subsequently all samples showed very high irreversibility fields (see in the Fig. 1). This implies a direct link between the pinning enhancement and the particular sample microstructure. An independent proof of the twin role was a slight depression of the secondary peak on its low-field side (Fig. 3). On the basis of angular experiments such a depression was identified with twin boundary effect [11]. Also in this sample the anomaly disappeared after the applied field had been declined from twin planes [12]. In twinned single crystals, however, one cannot see such a pronounced increase of Jc and Birr. Therefore conclude that the particular material microstructure composed of nano-lamellar, the structural modulation, an appropriate concentration of secondary phase particles, and a point-like disorder represent a new specific pinning structure effective especially at high fields.

The modulation and nanometer-scale lamellar structures are also found through the analysis by STM (see Fig. 6). The low magnification (see left figure) STM clearly shows that the modulation layers have the width around 3.5 nm, which is comparable to the coherence length [13]. EDX analysis identified these layers are RE1+xBa2−xCu3Oy. STM observation also confirmed that such lamellar structure was absent in the sample with 40 mol% NEG-211 (see right figure). However, the clusters of 3 to 4 nm diameter are dispersed in the 123 matrix. We therefore conclude that the lamellar structure provides a high density of pinning sites that are active especially at high fields.

As the average spacing of the nano-scale lamellae is 3.5 nm, and comparable to the coherence length (in YBCO ξ (77 K) ≈ 4.5 nm) [13], such a structure can principally
change the vortex dynamics and the effectiveness of pinning especially at high fields and temperatures. A pin defect extended at least in one dimension along the field direction (columnar track, void, twin plane etc.) is naturally more effective than a row of randomly distributed point-like pins along a single vortex line, due to much larger effective interaction volume of the pinned vortex. On the other hand, it is well known that presence of a twin structure does not necessarily result in an overall enhancement of critical currents. The channeling effect of twins leads to a redistribution of the current flow and appearance of additional in-plane anisotropy in the sample [11], which usually results in a suppression of \( J_c \) in the region of the secondary peak. The irreversibility field enhancement in presence of a twin structure is commonly observed but is not much significant. The novel nano-scale lamella structure has to act on vortices in a similar manner as conventional twins. It is probably the much higher density that makes this type of defects so effective at high fields. Most probably, vortex lattice transformations at high fields are shifted to higher fields. The actual roles of twin, lamella, and point-like pinning disorder are the subject of further investigation. A plate-like structure observed in heavily Pb-doped \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y \) single crystal [14] also significantly enhanced \( J_c \) and \( B_{irr} \) in accord with the present work.

IV. SUMMARY

The ternary melt–processed material with the \( \text{Nd:Eu:Gd} \) matrix ratio of 33:38:28 added with 5 mol\% of NEG-211 exhibited the irreversibility field exceeding 14 T and the secondary peak critical current density (\( J_c \)) of 70 kA cm\(^{-2}\) in 4.5 T at 77 K (\( H \parallel c \)-axis). The present results suggest that the improved flux pinning at high fields is due to the regular arrays of nonstoichiometric clusters with an average spacing comparable to the coherence length, which provides unusually strong pinning at high temperatures.

REFERENCES


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