Dramatic improvement of high-field pinning in NEG-123 via structure modulation on nanometer scale

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Abstract

Properties of the recently developed (Nd0.33Eu0.38 Gd0.29)Ba2Cu3Oy system are reviewed. These include the superconducting, magnetic, microstructure and chemical analysis. New nanometer scale pinning medium and its creation via an appropriate choice of matrix chemical ratio are discussed. The magnetization measurements revealed an outstanding vortex pinning up to very high magnetic fields at 77 K. Microstructure analysis found a superconducting matter modulation and formation of a special nanometer-scale lamellar structure. Such a structure led to irreversibility enhancement at 77 K to 15 T. The present results promise real high-field applications of high- $T_c$ bulk materials.

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1. Introduction

Recent progress in the melt-texture technology of bulk high-temperature superconductors (HTSc) has created a basis for engineering applications [1-7]. For most power applications a high critical current density ($J_c$) and a high irreversibility field ($B_{irr}$) at liquid nitrogen temperature, 77.3 K, are required. The typical $B_{irr}$ values at 77 K for YBa$_2$Cu$_3$O$_y$ (Y-123) are in the range of 3 - 5 T for $B||c$ [8-9]. $B_{irr}$ represents a limit for practical applications of the superconductor. It is a structure sensitive parameter reflecting efficiency of fluxoid (vortex) pinning in the superconductor at high magnetic fields. It shows that only defects comparable in size to vortex diameter are effective pinning centers in high fields. Vortex diameter at 77 K is about 4.5 nm [10]. This means that one needs to distribute a large amount of such small defects over the superconducting matrix. However, the elementary pinning energy is proportional to the defect volume and thermal activation energy at 77 K is rather high. Vortices can there fore easily escape from the small defects. Hence, an enhancement of pinning at very high fields and temperatures has met quite big obstacles and an increase of $B_{irr}$ has been difficult. Here we show that there is a way how to overcome these obstacles and arrive at an effective pinning structure operative at very high fields up to 77 K.

2. Experimental

High-purity commercial powders of Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$ and CuO were mixed in a nominal composition of (Nd$_{0.13}$Eu$_{0.38}$Gd$_{0.59}$)Ba$_2$Cu$_3$O$_y$. The starting powder mixtures were thoroughly ground, calcined at 880°C for 24 h with intermediate grinding, pressed into pellets and sintered at 900°C for 15 h under oxygen partial pressure (pO$_2$) of 0.1 % O$_2$. The whole procedure was repeated three times. Then commercial Nd$_4$Ba$_2$Cu$_2$O$_{10}$ (Nd-422), Eu$_2$BaCuO$_3$ (Eu-211), and Gd$_2$BaCuO$_3$ (Gd-211) powders were mixed in the ratio 1: 1: 1 and added to the sintered powders of NEG-123 in the concentrations 0 and 40 mol% of (Nd,Eu,Gd)$_3$BaCuO$_3$ (NEG-211), together with 0.5 mol% of Pt for the refinement of the 211 phase particles. In the next set of samples we added 0-10 mol% Gd-211 and 0-10 mol% (Eu,Gd)-211 to the NEG-123 powders.

Finally, pellets of 20 mm diameter and 15 mm thickness were prepared by cold isostatic pressing at 200 MPa. All samples were fabricated by the oxygen-controlled-melt-growth (OCMG) process at pO$_2$ of 0.1 % and gas flow rate of 300 ml/min. Details of the heat treatment schedule can be found elsewhere [11,12].

For magnetic measurements small specimens with dimensions of $a \times b \times c \approx 1.5 \times 1.5 \times 0.5$ mm$^3$ were cut from the as-grown pellets 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 down 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.

The microstructure features of these samples were studied with scanning electron microscope (SEM), transmission electron microscope (TEM), high-resolution electron microscope (HREM), dynamic force microscope (DFM), and scanning tunneling microscope (STM). Chemical composition of the matrix was analyzed by energy-dispersive X-ray spectroscopy (EDX). $T_c$ was determined from the temperature dependence of magnetic moment measured by means of a commercial SQUID magnetometer (Quantum Design, model MPMS7) at 1 mT. Magnetization hysteresis loops
(MHL) in fields from -2 to +7 T were measured by SQUID at 77 K. To minimize field inhomogeneity, the scan length was restricted to 10 mm. The samples exhibiting irreversibility field at 77 K beyond the SQUID maximum field were measured by means of VSM with maximum field of 14 T. In all cases the external magnetic field was applied parallel to the c-axis of the samples. Magnetic \( J_c \) values were estimated using the extended Bean's critical state model, \( J_c = 2(\Delta m/[a(d(b-a)/3)]) \), where \( d \) is the thickness, \( a \), \( b \) are transverse dimensions of the sample, \( b > a \), and \( \Delta m \) is the difference of magnetic moments on the descending and ascending field branch of the MHL, respectively [13].

3. Transition temperature

One of the most important characteristics, speaking about quality of the superconducting material, is the shape and position of superconducting transition. For the OCMG samples of LRE-123 material (LRE= light rare earth) high \( T_c \) over 93 K, and a narrow superconducting transition, below 1 K, are typical [14, 15]. Figures 1 show temperature dependences of the normalized magnetic susceptibility in zero-field-cooled (ZFC) and field-cooled (FC) modes in magnetic field of 1 mT for (Nd_{0.35}Eu_{0.38}Gd_{0.28})Ba_{2}Cu_{3}O_{y} superconductors with 5 and 10 mol\% NEG-211. Both samples exhibited sharp superconducting transitions less then 1 K wide. Similar superconducting transitions were found in all investigated samples [16]. These results indicate that samples are of a pseudosingle-crystalline nature.

![Figure 1. Temperature dependence of the normalized magnetic susceptibility for OCMG-processed (Nd_{0.35}Eu_{0.38}Gd_{0.28})Ba_{2}Cu_{3}O_{y} sample with 5 and 10 mol\% NEG-211 contents.](image)

4. Magnetization measurements
(a) NEG-123 with NEG-211 (SQUID experiment)

In Figure 2 curves of field-dependent magnetic moments, \( \Delta m \), measured by SQUID at 77 K on (Nd_{0.35}Eu_{0.38}Gd_{0.28})Ba_{2}Cu_{3}O_{y} samples with 0 to 40 mol\% NEG-211, with applied field parallel to the c-axis are plotted. With increasing NEG-211 content irreversibility field rapidly increased, reached maximum, and decreased again. The highest
irreversibility field exceeded 7 T, and the secondary peak position was around 3.6 T. This was achieved for NEG-211 content less or around 10 mol% (see left Fig. 2). With NEG-211 content above 10 mol%, the irreversibility field decreased to around 7 T (see right Fig. 2). The maximum $B_m$ was observed in the sample with 5 mol% NEG-211. It seems that the externally added LRE-211 influences chemical composition of the NEG-123 matrix during the melt-growth process [17, 18]. Recent results on the NEG-123 system with varying ratio of Nd:Eu:Gd in the superconducting matrix clarified that the matrix chemical composition can play an important role in improvement of flux pinning at high fields at 77 K [19].

(b) NEG-123 with Gd-211 (SQUID experiment)

In another experiment we maintained matrix chemical ratio as above (Fig. 2) but used instead of NEG-211 another secondary phase, Gd-211. The Gd-211 content ranged from 2 to 10 mol%. All six samples of this series again exhibited very high irreversibility fields at 77 K, H//c-axis (Fig. 3). Most samples showed nearly field independent $M(H_x)$ curve up to 4 T, which is a very promising result for high-field applications. Irreversibility field again increased with increasing Gd-211 content up to maximum for 5 mol% and then decreased in a similar way as with NEG-211.

Similar $M(H_x)$ properties were obtained for the samples cut form various locations of the pellet, showing a good reproducibility [20].

(c) NEG-123 with (Eu,Gd)-211 (SQUID experiment)

In order to verify the role of secondary phase in enhancement of irreversibility field, we changed the Gd-211 phase for (Eu,Gd)-211. Matrix chemical ratio was left same as above. Figure 4 shows $\Delta m(H_x)$ curves measured by SQUID at 77 K ($H_x$//c-axis) for (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ samples with 0 to 10 mol% (Eu,Gd)-211. Again, all
the samples exhibited the irreversibility field exceeding 7 T. Again, the samples with small secondary phase contents, 3 and 5 mol% showed the highest irreversibility field. We can thus conclude that in all studied series of samples with the chemical ratio Nd:Eu:Gd=33:38:28 the most favorable content of secondary phase, leading to the highest irreversibility field, was 5 mol%, irrespective of the secondary phase type.

(d) $\Delta m$-$H_a$ properties studied by VSM

In the samples with small amounts of secondary phase irreversibility field was always beyond the experimental field range of the SQUID. In order to see the actual $B_{irr}$ values at 77 K, we measured hysteresis loops of the (Nd$_{0.13}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ samples with 3 and 5 mol% NEG-211 by means of a vibrating sample magnetometer (VSM) with maximum field of 14 T. The field sweep rate was 0.6 T/min and magnetic field was again applied parallel to c-axis of the samples. The results are shown in Figure 5. The secondary peak of the sample with 3 mol% NEG-211 laid above 4 T, irreversibility field was around 12.5 T (see left inset of Figure 5). In the other sample, irreversibility field was higher than 14 T (see right inset of Fig. 5). Extrapolation of the $B_{irr}(T)$ dependence from higher temperatures to 77 K implied $B_{irr}(77 \text{ K}) \approx 15 \text{ T}$ [21]. This is the highest secondary peak position and the irreversibility field reported so far for melt-processed or single crystalline LRE-123 superconductors at this temperature. This represents a maximum field-trapping potential at the engineering temperature of 77 K.
5. Super-current density ($J_c$)

The super-current density, $J_c$, in the $(a,b)$-plane obtained from the extended Bean model is presented in Fig. 6. The values associated with the secondary peak reached 70,
49, and 22 kA/cm² at 4.5, 7, and 10 T, respectively (VSM data with field sweep rate 0.6 T/min.). The \(J_c(B)\) curves in Fig. 6 (right) show two distinct secondary peaks, PE1 and PE2, the typical result of a combination of a point-like pinning structure with twin plains. This can also be interpreted as a regular secondary peak due to point-like defects flattened by twin structure activity [22]. The temperature scan shows that PE2 (or the low-field edge of the secondary peak flattening) with increasing temperature only insignificantly shifts to lower fields but becomes more pronounced.

On the other hand, PE1 (the high-field edge of the secondary peak flattening) rapidly diminishes with increasing temperature and shifts to lower fields as a regular secondary peak. As only PE1 comes close to PE2, both peaks merge and the resulting singular peak (no more flattened or otherwise modified) shifts to lower fields and finally disappears. Similar effects have also been observed in twinned Nd-123 single crystals [23]. Angular experiments proved that the deformation of the MHLs was really due to a planar pinning structure aligned with \(c\)-axis.

6. Microstructure analysis

For understanding the exceptional magnetic performance of the \((Nd_{0.33}Eu_{0.38}Gd_{0.32})Ba_2Cu_3O_y\) samples microstructure study was of a primary importance. In this section we demonstrate the material microstructure as studied by various techniques.

(a) Transmission electron microscopy (TEM)

Figure 7 shows the dark-field TEM image of the sample with 5 mol% NEG-211 viewed from [001] direction (see left figure). Important feature of this image is the modulated structure within the twin walls. It has a twin-like structure but the spacing is much finer, of order of few nanometers. This structure was observed in the whole sample,
sometimes straight, sometimes wavy. A similar structure, indicated by white lines inside the normal twins, was also observed in the sample with 10 mol% NEG-211 (see right Fig. 7). This sample also showed rather high irreversibility field, over 11 Tat 77 K ($H_\text{irr}$)[c-axis].

(b) High resolution transmission electron microscope (HREM)

Figure 8 shows the HREM image of the (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ sample with 10 mol% NEG-211. The twin planes crossed at right angles, indicating that the c-axis was oriented perpendicular to the top surface. It was difficult to distinguish twin boundaries from anti-phase boundaries (APBs). Similar to twin boundaries, the APBs also produce a different diffraction contrast due to the strain at the boundaries [24]. Moreover, twin activity (flattening of the MHL) was not recognized in magnetic data of this material. This might be consistent with several reports stating that the twin activity drops with increasing amount of the secondary phase [25, 26]. In any case, to confirm character of the fine twin-like structure in this material and understand its role in magnetic studies, further experiments are needed.

![Figure 8. High resolution TEM images of (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ sample with 10 mol% NEG-211. Fine twin planes cross each other at right angles.](image)

(c) Atomic force microscopy (AFM)

Figure 9 shows an AFM image of the sample with 5 mol% NEG-211 viewed from <001> direction. One can see the modulation structure similar to that observed by TEM (Fig. 7). This confirmed the existence of the novel pinning structure in the materials with enhanced magnetic properties.

(d) Dynamic force microscopy (DFM)

To check correlation between the fine lamellar (or nano twin) structure and the good magnetic performance, we studied two sets of (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ samples, with a high and low irreversibility field. Figs. 10 and 11 show the DFM images of the samples with 3 and 5 mol% NEG-211 viewed from the <001> direction. In both samples a modulation structure and fine lamellas were observed inside regular twins. The lamellar
structure had the period of a few nanometers and ran along the normal twins. The lamellas were sometimes straight, sometimes wavy. This is in accord with TEM observations (Fig. 7). In both samples the high irreversibility field, above 12.5 T at 77K, $H \parallel c$-axis, was detected. On the other hand, no lamellas or matrix modulation were observed in the sample with 40 mol% NEG-211 (Fig. 12). This sample had irreversibility field about 7 T (Fig. 1.), similar to the regular LRE-123 materials.

The nano-scale lamellar structure systematically appeared in samples with 3 – 7 mol% NEG-211, the compounds exhibiting very high irreversibility fields. On the other
Figure 11. Dynamic force microscope images of (Nd_{0.8}Eu_{0.2}Gd_{0.28}) Ba_2Cu_3O_y sample with 5 mol% NEG-211. Modulation and island formation in the 123 matrix are visible.

Figure 12. Dynamic force microscope images of (Nd_{0.8}Eu_{0.2}Gd_{0.28}) Ba_2Cu_3O_y sample with 40 mol% NEG-211 prepared in 0.1% pO_2. Nanometer-scale lamellar structure was absent.
hand, the lamellas were not found in samples with NEG-211 content higher than 10 mol\% [27]. These materials exhibited significantly lower irreversibility field of about 7 T at 77 K. All these facts indicate that the observed pinning enhancement at high fields is due to the nano-scale lamellar arrays.

(e) Chemical analysis by TEM-EDX

A detailed information on the character of material microstructure was obtained by transition electron microscopy coupled with energy dispersive X-ray analysis (TEM-EDX). During this analysis the sample surface was scanned in discrete steps of 5 nm across the nano-lamella system. Diameter of the analyzed spot was about 2-3 nm. The (NEG)/Ba ratio regularly oscillating between 0.48 and 0.53 was observed (see Fig. 13). The finite size of the analyzed areas might slightly influence the results so that in reality even higher chemical ratio differences between lamellas and the neighboring matrix could be expected. In the TEM-EDX experiment the lamella array period was evidently close to the scanning step, i.e. about 5 nm.

![Graph showing oscillating values of (Nd+ Eu+ Gd)/Ba ratio](image)

**Figure 13.** TEM with EDX analysis of the material from Fig.11. Higher and lower values of the (NEG)/Ba ratio regularly vary with the step of 5 nm between extremes 0.485 and 0.515. Diameter of the analyzed spot was about 3 nm.

(f) Scanning tunneling microscopy (STM)

A further test of the microstructure on a nanometer scale was made by an ultra-high vacuum STM. Fig. 14 show microstructure of (Nd$_{0.13}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ sample with 5 mol\% of NEG-211. In Fig. 14 (left) matrix modulation is seen, in Fig. 14 (right) the nano-lamellar structure appears. The modulation period is about 4 nm, which is comparable to the coherence length (in YBCO (77 K) = 4.5 nm). Such a structure can principally change the vortex dynamics and pinning efficiency at high fields. A careful check of Fig. 14
(right) revealed a nano-lamellar structure along the modulation direction. No structure of this kind was identified in the sample with 40 mol% NEG-211 (Fig. 15). The samples exhibited very high and moderate irreversibility field, respectively.

Tunneling current spectra taken on the RE-rich clusters and the regular matrix (white and dark spots in Fig. 14, respectively) showed a similar conductivity of both parts. This was not much surprising as the composition of the RE-rich clusters was not much different from the NEG-123 matrix around.

**Figure 14.** STM image of the cleaved surface of (Nd$_{0.31}$Eu$_{0.18}$Gd$_{0.20}$) Ba$_2$Cu$_3$O$_y$ sample with 5 mol% NEG-211. The tunneling conditions were $V_s = 10$ V, $I_t = 0.3$ nA. Note the island structures formation, with the average period around 3.5 nm. Image of matrix modulation (left figure), nano-scale lamellae (right figure).

**Figure 15.** STM image on the cleaved surface of (Nd$_{0.31}$Eu$_{0.18}$Gd$_{0.20}$) Ba$_2$Cu$_3$O$_y$ sample with 40 mol% NEG-211. The tunneling conditions were $V_s = 10$ V, $I_t = 0.3$ nA. Only a few nanometer-size island structures, no sign of modulation were observed.
7. Pinning mechanism

The above structural analysis seems to present a quite reliable picture of the new pinning medium. Now we can speculate on the pinning mechanism associated with this new structure. First, we have to bear in mind that this nano-structure co-exists with regular twins. This raises the question if the observed enhancement of \( B_{ir} \) cannot be attributed to the effect of twins. It is well known that twins represent strong barriers for magnetic flux motion that might be effective up to high fields and temperatures. It has been, however, many times reported in literature that although the twin structure helps to extend MHL to higher fields, this extension is only slight. It is therefore not much probable that the regular twins themselves are responsible for the MHL extension.

The (NEG)Ba\(_2\)Cu\(_3\)O\(_y\) samples studied in this work were optimally oxygenated, hence the effect of oxygen deficiency was strongly suppressed. The nature of individual nano-scale pins in the present material does not differ from that in other LRE-123 compounds. The width and spacing of the nano-lamellas are comparable to coherence length (in YBCO \( \xi_{coh} \) (77 K) = 4.5 nm). Individual randomly distributed point-like pins of such a size arising from oxygen deficiency [8], Ba-rich clusters [28], RE-Ba solid solution [29, 30] have been associated with the secondary peak effect. This type of defects thus represents a pinning medium active at high fields but these fields are typically of a few Tesla. What contradistinguishes the pinning mechanism of the new structure from that of individual point-like pins of a similar size? The only difference seems to be in the defect organization and probably also in the alignment with regular twins. We suggest that the dense lamellar structure filling the space between regular twin planes slows down or even prevents the vortices channeling along regular twins. This mechanism can also shift the high-field vortex lattice transformation to even higher fields. We note that a nano-lamellar array was also observed in Y-123 single crystals [31] and another nanometer-scale plate-like structure was produced in a heavily Pb-doped Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_y\) single crystal [32]. They also significantly enhanced \( J_c \) and \( B_{ir} \) in accord with the present work. This technology can be easily adapted for mass production of high-\( T_c \) superconducting 'permanent' magnets for use in magnetic separation equipment for water purification, in magnetically levitated trains, high field superconducting generators, etc.

8. Conclusion

In conclusion, we found a new type of nanometer-scale lamellar pinning structure (nano-twins) in (Nd\(_{0.33}\)Eu\(_{0.38}\)Gd\(_{0.28}\))Ba\(_2\)Cu\(_3\)O\(_y\) superconductors with a small amount of a secondary phase. In principle, it is a modulation of the NEG-123 matrix composed of a regular and NEG/Ba-rich material in the form of lamellas aligned with regular twin structure. Having a very small period of a few nanometers, this new pinning phase represents a fine substructure of regular twins. The coincidence of presence of this structure in different samples with extremely high irreversibility field made us to believe that just this pinning medium is responsible for the outstanding electro-magnetic properties of these ternary superconductors at 77 K. This type of pinning structure appears in a narrow interval of Nd:Eu:Gd chemical ratio, around 33:38:28. Optimum properties were achieved for an appropriate small amount of secondary phase, from 3 to 7 mol\%. The structural analyses made by TEM, DFM, and STM showed the superconducting matter modulation and nano-lamellar structure formation. The high magnification STM showed that the lamellas are rows of aligned clusters of 3 to 4 nm in size. Such new pinning
centers led to a factor two improvement of $B_{irr}$, up to 15 T at 77 K and $H_d\parallel c$-axis. In accord with that, the secondary peak was observed as high as 4.5 T. The super-current density reached 70, 49, and 22 kA/cm$^2$ at 4.5,7, and 10 T, respectively. In combination with the recent outstanding progress in reinforcement of RE-123 pellets [Tomita], our results pave way to real high-field applications, e.g. in magnetically levitated trains.

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