Superconductors for high-field use at 77 K

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Abstract

Magnetic measurements of \((\text{Nd}_{0.33}\text{Eu}_{0.38}\text{Gd}_{0.28})\text{Ba}_2\text{Cu}_3\text{O}_y\) showed an exceptionally high-irreversibility field. This feature was always correlated with the presence of a superconducting matter modulation and formation of a special nanometer-scale lamellar structure. High-magnification scanning tunneling microscope observations revealed that such nanoscopic lamellas consist of arrays of aligned NEG-rich clusters of 3–4 nm in size. Routinely prepared NEG-123 samples with Nd:Eu:Gd = 1:1:1 exhibit \(B_{\text{irr}}\) of around 7 T, while the material with Nd:Eu:Gd = 1:1.25:0.85 combined with addition of 5 mol% 211 secondary phase exhibits the irreversibility line above 14 T at 77 K \((H_{\|}|c\text{-axis})\).

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1. Introduction

Large efforts have been devoted to the enhancement of the irreversibility field, \(B_{\text{irr}}\), since it sets the maximum field for practical applications. In YBa\(_2\)Cu\(_3\)O\(_y\) (Y123), typical \(B_{\text{irr}}\) values were in the range of 3–5 T for \(H_{\|}|c\text{-axis}\) at 77 K [1]. NdBa\(_2\)-Cu\(_3\)O\(_y\) (Nd-123) material fabricated with the oxygen-controlled melt-growth process exhibited \(B_{\text{irr}}\) up to 9 T at 77 K [2]. Microstructure observation confirmed the presence of clusters of a few nanometer size dispersed in the Nd-123 matrix. They consist of Nd-rich Nd\(_{1+x}\)Ba\(_{2-x}\)Cu\(_3\)O\(_y\) (Nd-123ss) superconducting phase according to microchemical analyses. They play a role similar to oxygen deficient clusters in Y-123 single crystals and are thereby responsible for the formation of the secondary peak in the \(M(B)\) curve [2]. Strong flux pinning of a similar origin was also observed in other RE-123 (RE: Sm, Eu, Gd) materials [3] where the light rare earth elements form RE\(_{1+x}\)-Ba\(_{2-x}\)Cu\(_3\)O\(_y\) type solid solution. However, the secondary peak arising from such type of pinning defects lies in intermediate fields. Evidently, \(B_{\text{irr}}\) can be raised only by the introduction of defects that are active up to high fields. In single-crystalline Nd-123 with high-pressure oxygen treatment, \(B_{\text{irr}}\) of 12 T has been achieved [4]. We studied
several batches of NEG-123 samples with various Nd:Eu:Gd ratios [5] with extremely high-irreversibility field. Microstructure analysis revealed a new type of pinning centers on nanometer scale. Such new pinning centers led to a significant improvement of $B_{\text{irr}}$ at 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 the amounts corresponding to the nominal composition of (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$. The preparation procedure was the same as described in Ref. [5]. The samples added with 0–40 mol% of NEG-211 were subjected to the oxygen-controlled melt-growth process in flowing 0.1% $p$O$_2$/Ar at 300 ml/min. The details of the heat treatment profile can be found in Ref. [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 $^\circ$C [6]. Microstructure of these samples was studied with a dynamic force microscope (DFM), and a scanning tunneling microscope (STM). Magnetization hysteresis loops (MHL) were measured at 77 K using a SQUID magnetometer with the maximum field of 7 T and 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 critical state model [7].

3. Results and discussion

Fig. 1 shows magnetic hysteresis loops of (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ samples with 0–40 mol% NEG-211 at 77 K for $H_c||c$-axis measured with a SQUID magnetometer. For NEG-211 content less or around 10 mol% the irreversibility field always exceeded 7 T, and the secondary peak was observed at around 3.6 T. With NEG-211 content above 10 mol%, the irreversibility field stayed at 7 T. In another set of experiments we replaced NEG-211 by Gd-211 and (Eu,Gd)-211 powders. We found similar dependence of magnetic behavior on the secondary phase concentration in both sets of the samples as in the samples with NEG-211. We can thus conclude that the excellent high-field pinning is associated with the particular value of the chemical ratio in NEG-123 matrix combined with an appropriate amount of a secondary phase.

In order to determine the irreversibility field for the NEG-123 sample with 5 mol% NEG-211 at 77 K ($H_c||c$-axis), we measured hysteresis loops using a 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 modified Bean model [7] is presented in Fig. 2. The most remarkable feature of the newly developed NEG sample is the irreversibility field over 14 T (inset of Fig. 2). The secondary peak was located at around 4.4 T, and the $J_c$ values reached 70, 49, and 22 kA/cm$^2$ at 4.5, 7, and 10 T, respectively. Extrapolation of $B_{\text{irr}}(T)$ dependence from temperatures above 77 K implied the $B_{\text{irr}}$ value at 77 K was about 15 T [8].

DFM was used to observe microstructure with the aim of clarifying the source of the exceptionally superior magnetic performance of the (Nd$_{0.33}$Eu$_{0.38}$Gd$_{0.28}$)Ba$_2$Cu$_3$O$_y$ samples. Fig. 3(a)–(c) shows the
DFM images of the samples with 3, 5, and 40 mol% NEG-211 viewed from the \(001\) direction. In the two samples with lower concentrations of NEG-211 a modulation structure and fine lamellas were observed inside regular twins (see Fig. 3(a) and (b)). The lamellar structure had the period of a few nanometers and ran along the normal twins, sometimes straight and sometimes wavy. Similar features were also detected by TEM [8]. At the same time, both samples exhibited a high-irreversibility field, above 12.5 T at 77 K and \(H||c\)-axis. On the other hand, no lamellas or matrix modulation were observed in the sample with 40 mol% NEG-211 (Fig. 3(c)). This sample had the irreversibility field about 7 T (see Fig. 1). This represents a direct link of the enhanced pinning in high fields to the particular microstructure.

One can directly identify twin activity in the shape of hysteresis loops. The secondary peak is typically slightly depressed down to its low-field side (Fig. 2). Such a depression was identified as a consequence of a twin structure effect [9], in that magnetic measurements at different angles between applied field and twin planes results in different loop shapes. Also in the present samples the depression disappeared after applied field had been declined from twin planes by about 20° [10]. It is also evident that twin structure has no pronounced effect on \(B_{irr}\). We therefore conclude that the particular microstructure composed of nanoscopic lamellas and/or correlated structural modulation represents a new specific pinning structure effective especially at high fields.

STM identified the lamellar structure as arrays of interconnected clusters with diameter of 3–4 nm (Fig. 4, left). In the sample with 40 mol% NEG-211 individual clusters with the same diameter were found (Fig. 4, right). This also supports our conclusion that the lamellar structure is the relevant pinning medium which enhances the magnetic performance up to very high fields.

The channeling effect of twins leads to a redistribution of the current flow and appearance of an additional in-plane anisotropy in the sample [9]. This usually results in a suppression of \(J_c\) in the region of the secondary peak, sometimes filling the dip between central and secondary peaks [11]. The irreversibility field enhancement in samples with regular twins is commonly observed but is not so significant. The function of the novel...
nanometer-scale lamellar structure may be similar to conventional twins. However, the principal feature differentiating it from regular twin structure is the size and period comparable to the coherence length (in YBCO $\zeta_{ab}$ (77 K) $\approx$ 4.5 nm). These factors probably enable this structure to trap vortices effectively up to high fields and temperatures. Note that a plate-like structure observed in a heavily Pb-doped Bi$_2$Sr$_2$CaCu$_2$O$_y$ single crystal [12] also significantly enhanced $B_{irr}$ in accord with the present work. The actual role of twins, lamellas, and point-like pinning disorder require a further study.

We can conclude that a combination of the optimum matrix chemical ratio and quantity of secondary phase particles in the NEG system produces a specific matrix structure that leads to only a slightly field-dependent $J_c$ in a broad range of fields, supported by the high-irreversibility field. Applications of melt-processed materials have been so far restricted to fields of a few Tesla. The present results enable extension of the bulk superconductor applications at 77 K up to fields over 10 T.

4. Summary

The ternary melt-processed material with the initial Nd:Eu:Gd matrix ratio of 33:38:28 added with 5 mol% of NEG-211 exhibits the irreversibility field exceeding 14 T at 77 K ($H_{irr}$||c-axis) and the secondary peak in critical current density ($J_c$) of 70 kA/cm$^2$ at 4.5 T. The microstructure study together with magnetic measurements suggest that the improved flux pinning at high fields is due to the arrays of non-stoichiometric clusters with an average size and period comparable to the coherence length.

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