Study of superconducting properties of OCMG processed (Nd, Eu, Gd)–Ba–Cu–O with Pr doping

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Abstract

The superconducting and magnetic properties of oxygen-controlled-melt-grown (Nd, Eu, Gd)Ba$_2$Cu$_x$O$_{y-2x}$ (NEG-123) superconductors containing Pr in the concentration range $x = 0$ to 0.15 are reported. X-ray diffraction results confirmed the main phase as NEG-123 phase without any significant change in the crystal structure. Magnetization measurements revealed a depression of the superconducting transition temperature, $T_c$. The transitions are sharp at low Pr concentrations, however, a broad maximum begins to develop when the Pr concentration is $x > 0.1$. The critical current densities, $J_c$, and the irreversibility fields are found to decrease on increasing the Pr content. It is also found that $J_c$ of the Pr-doped composites for $x = 0.12–0.15$ is about five orders of magnitude lower than that of the pure NEG-123 composites. The fall in $T_c$ and $J_c$ on Pr doping is explained in terms of the partial substitution of Pr on the rare earth site and hole localization due to trivalent ions on the Ba site. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

For applications of high-$T_c$ superconductivity, there is still a considerable interest to increase the critical current density, $J_c$, even further. This is especially important at temperatures around 77 K aimed at in applications. The superconductors of the '123'-type (e.g., YBa$_2$Cu$_3$O$_y$) are still the best candidates for bulk applications at 77 K because of their relatively small anisotropy and the well-developed pinning properties.

Many concerted attempts have been made to enhance the critical current density by electron, neutron or heavy ion irradiation, and by means of chemical doping by Pt, Rh, Ag and Ni, etc. [1–6]. Pr is the only rare earth ion that can form a magnetic insulator and depress the superconductivity of the 123 phase. However, in contrast to this negative effect of Pr on the superconductivity, doping of YBa$_2$Cu$_3$O$_y$ by Pr has also been found to enhance the critical current densities at low Pr concentrations [7,8].

For a detailed understanding of the effects caused by chemical doping and irradiation, it is important to regard the underlying microscopic pinning mechanisms. In high-$T_c$ superconductors with their large $\kappa$-values, two basically different pinning mechanisms can act: The $\delta$-pinning which provides a scatter of...
the carrier mean free path (i.e., pinning at normal-conducting inclusions), and the $\delta T_c$-pinning based on a spatial variation of the transition temperature, $T_c$ [9].

For the case of various YBa$_2$Cu$_3$O$_y$ (YBCO) thin films, Griessen et al. [10] concluded that the $\delta T_c$-pinning is the dominant pinning mechanism by means of an analysis based on the General Inversion Scheme. Van Dalen et al. [11] reached the same conclusion for a twin-free DyBa$_2$Cu$_3$O$_y$ single crystal. However, recently in Pr-doped YBCO thin films [12] and (K, Ba)BiO$_3$ [13], the opposite conclusion was drawn. The Pr-doping (Pr concentration denoted by $x$) was found to yield an increase of the current densities, $J_c$, and of the pinning potential, $U_p$, only in a narrow region with $x$ ranging between 0.05 and 0.1.

The analysis of pinning forces from a wide range of literature data showed that just such a $\delta T_c$-pinning mechanism is very effective to provide both an increase of $J_c$ and of the pinning potential $U_p$ and hence, a considerable reduction of flux creep effects at elevated temperatures [14]. Therefore, this pinning mechanism is very important for a further improvement of the critical current densities at $T = 77$ K. However, it is still needed to understand the properties of this kind of pinning, and its relation to the microstructure.

In the recently developed (LRE)Ba$_2$Cu$_3$O$_y$ (LRE-123) superconductors (LRE = light rare earth atoms), just such a $\delta T_c$-pinning [9] (or $\Delta \kappa$-pinning [15–17]) mechanism was found to be active by means of a scaling analysis of the volume pinning forces [14]. In the LRE-123 system, the spatial variation of $T_c$ is provided by composition fluctuations caused by a solid solution between the LRE atoms and Ba. A further improvement of $J_c$ is obtained in ternary compounds, where three LRE atoms are mixed together on the rare earth site, e.g., (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ (NEG-123) [18]. In Ref. [19], we ascribed this improvement of the $\delta T_c$-pinning to a better, more uniform distribution of the $\delta T_c$-pinning sites throughout the sample, thus providing a constant pinning wavelength. One possibility to further enhance this effect would now be to increase the disorder by adding a fourth rare earth element to the system. As a candidate for this experiment, we selected Pr, as there is a considerable effect of Pr on superconductivity. This topic is currently quite extensively discussed in the literature [20–22], especially if it is possible to prepare a superconducting PrBa$_2$Cu$_3$O$_y$ under special preparation conditions. As our OCMG process is optimized so to reduce the substitution of the LRE atoms on the Ba site, we should see a clear effect of the Pr-doping on the superconducting properties of NEG-123.

Therefore, the aim of this investigation is to use the Pr-doping as a tool in order to strengthen the $\delta T_c$-pinning, and hence to improve the critical current densities. In order to have control over the microstructure which may change by means of the Pr-doping, local flux distributions were studied as well. For this purpose, we employed magneto-optic imaging [23], which is the best-suited tool for such quality checks of superconductors [24,25]. To the best of our knowledge, a systematic study of the field dependencies of the critical current densities as a function of Pr content in OCMG-processed LRE-123 systems has not been reported so far.

2. Experimental details

High-purity commercial powders (99.99% purity) of Pr$_2$O$_3$, Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$ and CuO were weighed to have a nominal composition of (Nd, Eu, Gd)$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-\delta}$, in which the Pr content $x$ varies from 0 to 0.15. The nominal mixture of Nd:Eu:Gd = 1:1:1. In a first step, precursor powders were prepared. The starting powders were ground thoroughly and calcinated at 880°C for 24 h with intermediate grinding, and pressed into pellets. The sintering was carried out at 1020°C for 48 h. This entire process was repeated three times.

The precursor powders were pressed into pellets with a diameter of 20 mm and a thickness of 15 mm, which were subjected to cold isostatic press (CIP) with a pressure of 2000 kg/cm$^2$. A MgO (100) seed was placed on the center of the pellet, which was subsequently OCMG-processed in 0.1% partial pressure of O$_2$ with a gas flow rate of about 300 ml/min. The details of the heat treatment schedule can be found elsewhere [18].

For oxygen annealing, samples with dimensions $(a \times b \times c) = 1.5 \times 1.5 \times 0.5$ mm$^3$ were cut from the as-grown crystals and annealed in flowing O$_2$. 


gas in the temperature range of 300–600°C with the following heat treatment schedule. The samples were heated to 600°C in 2 h, held for 1 h and cooled to 500°C in 12 h, then to 400°C in 24 h, and finally to 300°C in 24 h and held there for 100 h, and subsequently followed by furnace cooling.

The structural characterization was carried out using a powder diffractometer equipped with a rotating Cu anode X-ray tube and Cu-Kα radiation. Magnetization hysteresis loops (MHLs) were measured at 77 K in applied fields up to 7 T using a commercial SQUID magnetometer [26]. The magnetic field was applied parallel to the c-axis. The superconducting transitions (ZFC, FC) were measured with an applied magnetic field of 1 mT. Critical current densities were evaluated from the hysteresis data based on the extended Bean critical state model [27].

Flux distributions were obtained by means of magneto-optic (MO) imaging. MO imaging was recently reviewed in Ref. [23], so a short summary suffices here. This technique is based on the Faraday effect in a magneto-optically active material. The MO images presented here are maps of the z-component of the local magnetic field, \( B_z \), and increasing brightness corresponds to increasing values of \( B_z \). As magneto-optical active layer, we employed a Bi-doped YIG (yttrium–iron–garnet) film with in-plane anisotropy. The magnetic field (\( H_{max} = 500 \text{ mT} \)) is generated by a copper solenoid, also applied parallel to the c axis of the samples.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the NEG-123 samples containing Pr in concentrations \( x \) ranging between 0 and 0.15. An examination of Fig. 1 reveals that the samples mainly consist of the NEG-123 phase along with a small amount of second phase NEG-211. The intensity and peak positions of the prominent peak reflections are in good agreement with our earlier results [18]. The unit cell dimensions were determined from the observed \( d \) spacing using the least squares method assuming the structure orthorhombic. The lattice constant ratios \( a/b \) and \( c/b \) and the unit cell volume \( V \) are listed in Table 1. It is interesting to note that the crystal structure remains nearly the same in all samples. These results demonstrate that there is no significant effect on the crystal structure by substituting NEG-123 by Pr, which is identical to the GdPr systems studied in Ref. [28].

Fig. 2 displays the temperature dependence of dc magnetic susceptibility for the Pr-doped NEG-123 samples in zero-field-cooled (ZFC) and field-cooled (FC) processes in the presence of a magnetic field of 1 mT. From Fig. 2, it is evident that the \( T_c \) (onset) decreases with Pr concentration, i.e., from 94.1 K for \( x = 0 \) to 83 K for \( x = 0.15 \). For low concentrations of Pr \((x < 0.8)\), \( T_c \) gets slightly depressed, but the superconducting transitions are still quite sharp. However, a broad maximum begins to develop just above \( T_c \) for \( x > 0.1 \). All the samples \((x < 0.1)\) show a transition width of 2 to 3 K thus proving the

![Fig. 1. XRD patterns for the (Nd, Eu, Gd)\textsubscript{1-x}Pr\textsubscript{x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y} composites OCMG-processed in 0.1% \( p(\text{O}_2) \).](image-url)
Table 1
The lattice parameters and $T_{\text{onset}}$ (onset) for different $x$

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<th>$c/b$</th>
<th>$V\times10^{-15}$ m$^3$</th>
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relatively good quality of the samples. These results are consistent with the earlier investigations on Pr-doped YBCO systems [8]. It is an established fact that Pr on the rare earth site in Pr-doped YBCO compounds does suppress superconductivity. The suppression of $T_{\text{c}}$ has been attributed to two possibilities: the Abrikosov–Gorkov pair breaking effect or hole localization and filling. Both effects may be due to the hybridization of the Pr ion with the neighboring CuO$_2$ planes. Neutron diffraction data of the R(Ba$_{1-x}$R$_x$)$_2$Cu$_3$O$_{7+\delta}$ (R = Pr, Nd) system refined by the Rietveld method indicated that the depression of superconductivity is due to two independent effects, (i) Pr on the R site and (ii) hole localization due to trivalent ions on the Ba site; Pr on the Ba site appears to behave like all the other trivalent R ions [29].

Fig. 3 shows MHLs of Pr-doped NEG-123 measured at $T = 77$ K, $H_{\text{c1}}||c$. It is clearly visible that all the samples with $x < 0.10$ exhibit the secondary peak effect. This indicates that the field-induced pinning centers (that is, $\delta T_{\text{c}}$-pinning) are active in these systems like in the other LRE-123 systems fabricated by the OCMG process [18,30–32]. Note that the magnetization $M$ decreases rapidly with Pr contents above 0.10.

The critical current densities calculated by using Bean model formula are shown in Fig. 4. It is evident that the peak current, $J_{\text{peak}}$, and the irreversibility fields are systematically decreasing with increasing the Pr content. Furthermore, the peak position shifts to lower fields on increasing Pr concentration. This behavior is completely different as compared to the addition of NEG-211 or Gd-211 particles to the system [33–35]. The critical concentration of $x$ required to suppress the peak, is estimated to be around $x = 0.12$ (77 K, $H_{\text{c1}}||c$). In
addition, the peak height reduces continuously on increasing the Pr-doping. This indicates that just the mechanism responsible for the peak formation is affected by the Pr-doping. These results indicate that the suppression of $T_c$ and peak $J_c$ with Pr ions involves more than just introducing disorder into the system.

Similar phenomena have also been observed by others [36] for epitaxial Pr-doped YBCO thin films prepared by pulsed-laser-deposition method. There,
it was found that the critical current decreases by more than two orders of magnitude as \( x \) changes from 0 to 0.30. This fall of \( J_c \) with \( x \) was explained semiquantitatively in terms of a simple model of depairing by impurity centers suppressing the order parameter out to a distance of the in-plane coherence length. On the other hand, Pr-doping in low concentrations was found to increase the pinning strength. Both the pinning energy at 27 K and the intragranular critical current density at 10 K exhibit maxima at \( x = 0.1 \) to 0.2, with values that are about twice the corresponding values at \( x = 0 \) [8]. Considering the high critical current densities and the collective nature of pinning it was proposed that the local lattice mismatch and related stress field play an important role for the enhancement of critical current densities and activation energy. Here, it is also important to note that the increase of \( J_c \) due to Pr-doping was found in thin films, which do not exhibit the peak effect in \( J_c(B) \).

The drastic decrease of \( J_c \) on Pr-doping could also be due to an increasing inhomogeneity (granular) on increasing the Pr content, i.e., the grain growth may be affected by the Pr-doping. To exclude this possibility, we performed magneto-optic imaging of the flux patterns at three different temperatures, 18 K, 50 K, and 75 K. These flux patterns are presented in Fig. 5. For this figure, we have chosen three different samples with \( x = 0.01 \) (upper row), 0.06 (middle row) and 0.12 (lower row). The samples are first cooled down in zero field, then a field of 330 mT is applied and subsequently removed in order to obtain the remnant state (\( H_s = 0 \)). Remnant states are very sensitive to the effects of granularity as discussed in Refs. [37–39]. In the relatively thin high-\( T_c \) superconductors, vortices of opposite polarity are generated already before reaching the remnant state, so these may eventually become stable and penetrate the sample. Such an effect is even enhanced in the presence of structural defects. Therefore, weak channels between well-shielded grains are scanned effectively when observing remnant states.

All samples are found homogeneous bulks, with no weak channels present. Therefore, the determina-

![Fig. 5. Flux distributions of the Pr-doped NEG samples at various temperatures. Shown is always a remnant state, obtained after applying a field of 330 mT and subsequently reducing it to zero. (a–c) present the sample with \( x = 0.01 \), (d–f) the sample with \( x = 0.06 \), and (g–i) the sample with \( x = 0.12 \).](image-url)
Fig. 6. Field dependence of the critical current density \( J_c \) values normalized by \( T_c \) for the (Nd, Eu, Gd)\(_{1-x}\)Pr\(_x\)Ba\(_{2}\)Cu\(_{3}\)O\(_y\) \((0.00 < x < 0.15)\) composites OCMG-processed in 0.1% \( \rho(\text{O}_2) \).

4. Conclusion

We have studied the effect of Pr addition on the superconducting properties and the field dependence of the critical current densities at 77 K for OCMG-processed (Nd, Eu, Gd)Ba\(_2\)Cu\(_3\)O\(_y\) composites. The XRD results indicate that all the samples predominantly have a single-phase RE-123 structure and there is no significant effect on the crystal structure. As a general trend, the superconducting transition temperature \( T_c \) decreases with increasing Pr concentration as in the case of the YBCO system. However, the depression of \( T_c \) is small for low Pr concentrations. Magneto-optic flux patterns revealed that all samples are homogeneous, so effects of increasing granularity on increasing Pr content can be excluded. The critical current densities are found to decrease monotonously on increasing Pr content; no effect of a strengthening of the \( \delta T_c \)-pinning is observed. The current density at the fishtail peak decreases by more than five orders of magnitude as \( x \) changes from 0 to 0.12.

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