Pinning enhancement by heterovalent substitution in $Y_{1-x}RE_xBa_2Cu_3O_7-\delta$

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Abstract

The intragrain pinning in high-$T_c$ superconductor compounds $Y_{1-x}RE_xBa_2Cu_3O_7-\delta$ with low concentration of RE (La, Ce, Pr) was investigated. Magnetic and transport measurements reveal that the pinning is maximal for the concentration of heterovalent RE such that the average distance between the impurity ions in the plane of rare-earth elements is close to the diameter of Abrikosov vortices in YBCO.

1. Introduction

Improvement of critical current of YBCO materials is attained by the creation of additional defects acting as pinning centers. Irradiation, incorporation of nanoparticles, and doping [1–5] are the main ways to increase the pinning. In the last case the partial substitution of rare-earth (RE) elements for Y is favorable [3, 6–9]; it results in local distortions of the crystal structure and electron density. In most cases, $Y_{1-x}RE_xBa_2Cu_3O_7-\delta$ was previously investigated with the concentration $x$ being about a few tens of atomic per cent. It is found that the pinning depends on the valence and size of the RE ions. Doping ions with valence $3+$ do not change the superconducting properties of YBCO significantly, unlike ions with larger valence [10]. An increase of pinning in $Y_{1-x}RE_xBa_2Cu_3O_7-\delta$ films with small concentrations of RE ($x < 0.1$) was reported in [8]. The authors of [8] were interested mainly in the relative influence of different doping elements on the flux pinning. They found a pinning enhancement with a minute amount of doping with different RE elements, especially Tb and Nd. The dependence of critical current density in polycrystalline $Y_{1-x}Pr_xBa_2Cu_3O_7$ on $x$ was investigated in [9]. The maximal critical current density was reached for $x = 0.08$.

To study the concentration dependence of pinning we suggest choosing $x$ in connection with the parameters of the crystal structure. The concentration of RE can be correlated with the average distance between impurity ions in the rare-earth plane, $D$. The $Y$ atoms are arranged in the planes in YBCO such that the connection between $x$ and $D$ is given by $x = a^2/D^2$, where $a$ is the lattice constant in the rare-earth plane. This can be written as $x = a^2/(na)^2 = 1/n^2$, where $n = D/a$. Thus one can choose $x$ to obtain integer $n = 2, 3, 4, 5, 6, 7, 8, 9, 10, \infty$, i.e. $D$ is divisible by $a$. The compound with $n = \infty$ corresponds to classical $YBa_2Cu_3O_7-\delta$. Such choice of $x$ reveals the pinning dependence on the average distance between the pinning defects.

To prove the influence of the heterovalent substitution on the pinning we investigated YBCO doped by Ce and Pr. Ions of Ce and Pr have valence equal to $4+$ and $3–4+$ correspondingly, and should strongly modify the superconductivity near their location. Ions of La have the same valence as Y, but a larger radius. Doping by La is chosen to examine the influence of lattice distortion without the distortion of electron density.

Earlier we published the first results for $Y_{1-x}Ce_xBa_2Cu_3O_7-\delta$ with the above-stated concentrations $x$ [11, 12]. Here we report a comparative study of the magnetic and transport characteristics of $Y_{1-x}Pr_xBa_2Cu_3O_7-\delta$, $Y_{1-x}La_xBa_2Cu_3O_7-\delta$ and $Y_{1-x}Ce_xBa_2Cu_3O_7-\delta$. Measurements of magnetization and resistance were carried out. This allows comparing the intragrain pinning in the compounds with different $x$.

2. Experimental details

Three series of compositions $Y_{1-x}RE_xBa_2Cu_3O_7-\delta$ were prepared for $RE = Ce$, Pr, La. The series ($Y_{1-x}Ce_xBa_2Cu_3O_7-\delta$, $Y_{1-x}Pr_xBa_2Cu_3O_7-\delta$ and $Y_{1-x}La_xBa_2Cu_3O_7-\delta$) were synthesized separately by the standard solid-phase technique. The starting reactants were $Y_2O_3$, $CeO_2$, $Pr_2O_3$, $La_2O_3$, $CuO$, and $BaCO_3$. The corresponding amounts of reagents were mixed thoroughly in an agate mortar, pelletized, and annealed...
at 930 °C. The synthesis, including seven intermediate crushings and pressings, lasted 160 h. Long procedures favor ordering of RE elements and cerium substitution in yttrium positions. Once the synthesis was completed, the samples were annealed at a temperature of 300 °C for 3 h and cooled slowly in the furnace to room temperature to reach oxygen saturation.

Each series contained 10 samples, with \( x = 0.25, 0.11, 0.0625, 0.04, 0.0278, 0.0204, 0.0156, 0.0123, 0.01 \) and \( 0 \), which were synthesized simultaneously at the same conditions. The chosen concentrations of RE correspond to \( n = 2, 3, 4, 5, 6, 7, 8, 9, 10 \) and \( \infty \). In such a way the composition with \( x = 0 \) \( (\text{YBa}_2\text{Cu}_3\text{O}_7)_x \) was synthesized for each series.

The temperature dependence of resistance \( R(T) \) was measured by the standard four-probe technique with the bias current 10 mA. Samples have rectangular cross section (2 mm × 1 mm), the distance between the potential contacts being 2 mm.

The magnetic characteristics were measured by a vibrating sample magnetometer. The samples were cut into cylinders with height \( \approx 5 \) mm and diameter \( \approx 0.5 \) mm. The temperature dependence of magnetization was measured for samples cooled without external field \( (M_{ZFC}) \) and in a magnetic field of 100 Oe \( (M_{FC}) \). The measurements were carried out during heating at the rate 0.8 K min\(^{-1}\) from 77.4 to 100 K for \( Y_1-x\text{Ce}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) and \( Y_1-x\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) and from 55 to 100 K for \( Y_1-x\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \). The magnetic field \( H = 100 \) Oe was applied parallel to the cylinder axis. The temperature of the intragrain superconducting transition \( T_c \) was determined from \( M_{ZFC}(T) \) (the criterion is \( dM/dT = 0 \)). The temperature of disappearance of resistance \( T_{c0} \) was determined from \( R(T) \) (the criterion is that the voltage drop on the sample = 1 \( \mu \)V cm).

### 3. Results and discussion

The x-ray diffractions patterns show that most of the samples are single phase, and have the YBCO structure. There are small distortions of crystal lattice for \( Y_1-x\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) with high concentrations of La \( (x = 0.11, 0.25) \). For \( Y_1-x\text{Ce}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) the phase BaCeO\(_3\) precipitates when \( x > 0.024 \) (see details in [12]) because Ce dissolves in YBCO at low concentrations only.

Figure 1 displays the temperature evolution of the resistance \( R(T) \) normalized to \( R(100 \) K) for a few samples. The measured \( R(T) \) dependences are typical for polycrystalline superconductors and exhibit a sharp drop of the resistance at \( T_c \) and a smooth part until \( T_{c0} \), reflecting the transition of Josephson media formed by the intragrain boundaries. Above \( T_c \) most of the \( R(T) \) dependences are metallic like. The exception is \( Y_{0.75}\text{La}_{0.25}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) \((n = 2)\), having a quasi-semiconductor like \( R(T) \) above \( T_c \). This is probably because La partially occupies Ba sites for high \( x \) [13]. The \( R(T) \) dependences demonstrate that Pr depresses the superconductivity more strongly than Ce or La. The remarkable tail from \( T_c \) to \( T_{c0} \) on \( R(T) \) of \( Y_1-x\text{Ce}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) for \( n = 3 \) shows that the intragrain boundary thickness is increased due to a precipitating of nonsuperconducting phase (see [14] concerning the composites YBCO + nonsuperconducting compounds).

Figure 2 demonstrates that \( T_c \) of \( Y_{1-x}\text{RE}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) depends weakly on the RE concentration for \( x < 0.0625 \) \((n > 4)\). To reveal the influence of RE impurities on the intragrain boundaries we compared the width of the superconducting transition \( (T_c - T_{c0}) \) of the samples. These widths were normalized to \( T_c \) for a correct comparison of samples with different \( T_c \). Figure 3 plots the normalized width of the superconducting transition \( (T_c - T_{c0})/T_c \) for the samples as a function of \( n \). The dispersion of \( (T_c - T_{c0})/T_c \) is \( \approx 4\% \) for compositions

![Figure 1. Temperature dependence of normalized resistance \( R(T)/R(100 \) K) of samples \( Y_{1-x}\text{RE}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \).](image-url)
Intrgrain critical temperature $T_c$ of $Y_{1-x}\text{RE}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The temperature dependences of magnetizations $M(T)$ for $Y_{1-x}\text{RE}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x = 0$ ($n = \infty$) has a maximal value at $T = 77.4$ K as a function of $n$. The shape of dependence $\Delta M(n)$ and the position of the maximum do not change at other $T < T_c$. The magnetization loops of samples are typical for polycrystalline superconductors. The $M(H)$ dependences of sample $Y_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x = 0.0156$ ($n = 8$) measured for different $H$ are presented in figure 4. There is a method [15] for separating the intragrain and intergrain critical currents from $M(H)$ curves measured up to low and high values of magnetic field. However, the width of the $M(H)$ loop at zero field is practically the same for curves measured up to 200 and 1000 Oe. Also the observed asymmetry of the $M(H)$ loop at high $H$ is a sign of the strong influence of the edge barriers [16, 17]. For such a case application of the Bean model and the method in [15] is incorrect [18].

The temperature dependences of magnetizations $M_{\text{ZFC}}(T)$ and $M_{\text{ZFC}}(T)$ of the samples at $H = 100$ Oe are plotted in figures 5(a)—(c). The samples $Y_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x = 0$ ($n = \infty$) has a somewhat smaller absolute values of $M_{\text{ZFC}}(T)$ at any fixed $T$ than $Y_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. For such a case application of the Bean model and the method in [15] is incorrect [18].

The magnetization loops of samples are typical for polycrystalline superconductors. The $M(H)$ dependences of sample $Y_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x = 0$ ($n = \infty$) has a maximal value at $T = 77.4$ K as a function of $n$. The shape of dependence $\Delta M(n)$ and the position of the maximum do not change at other $T < T_c$. The magnetization loops of samples are typical for polycrystalline superconductors. The $M(H)$ dependences of sample $Y_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $x = 0$ ($n = \infty$) has a maximal value at $T = 77.4$ K as a function of $n$. The shape of dependence $\Delta M(n)$ and the position of the maximum do not change at other $T < T_c$. For such a case application of the Bean model and the method in [15] is incorrect [18].

The discrepancy between our result for maximal pinning concentration and the result in [9] ($x = 0.08$) is possibly because the technique of synthesis used in [9] differs from ours. In the samples used in [9] the Pr doping partially goes to the intergrain boundaries, modifying them. This also leads to a decrease of the actual concentration of Pr in the granules. Therefore doping by RE elements with valence higher than 3+ is preferable for high pinning.
4. Conclusions

The resistance dependences on temperature of $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$ demonstrate that the RE impurities do not modify the intergrain transport when $x < 0.04$. The remanent magnetization of the samples reveals that doping with RE elements with valence higher than $3+\delta$ in small amounts increases the intragrain pinning. The doping of YBCO by the homovalent RE (La) does not increase the pinning. The concentration of the heterovalent RE for the maximal pinning, $x = 0.0156$, is the same for both tested elements (Ce and Pr). This concentration corresponds to the average distance between the impurity atoms, equal to 3.06 nm ($\sim 2\xi_0$).

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