Improvement of Flux Pinning Properties of RE123 Materials by Chemical Doping

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Abstract. Improvement of flux pinning properties of RE123 single crystals and melt-solidified bulks was attempted by dilute doping of impurity elements to various cation sites except the Cu at the CuO₂ plane. All the examined dilute doping for RE123, such as Sr to Ba-site, Lu to Y-site and Co to Cu-site in the CuO-chain, was found to increase critical current density, \( J_c \), particularly under magnetic fields accompanying enhanced second peak effect. These results suggest that the dilute doping is universally effective for improving the critical current properties of the RE123 system independent of the doped cation sites.

1. Introduction

It is well known that the \( \text{REBa}_2\text{Cu}_3\text{O}_y \) (RE123: \( \text{RE} = \text{Y}, \text{La}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu} \)) system exhibits high critical current performance under high magnetic fields at 77 K because of relatively low electromagnetic anisotropy and various pinning sites in the crystals. The RE123 melt-solidified bulks have been extensively used as for high-field bulk magnets and the RE123 coated conductors are expected to become the second generation conductor of high \( T_c \) cuprates. In the present system, various defects, such as oxygen vacancies, twin boundaries, local RE-rich regions and irradiation damages, can act as effective pinning sites. Furthermore, small amount of Zn doping for Cu in Y123 was reported to contribute to enhanced \( J_c \) characteristics [1]. In our previous study, small amount of Fe, Co or Ni doping for Cu in Bi(Pb)2212 single crystals was found to be also effective for enhancement of \( J_c \) [2]. This suggested that impurity doping directly for the superconducting CuO₂ plane is universally effective method to introduce point-defect-like pinning sites in the cuprate superconductors when the doping level is quite low. Such a "dilute doping" technique is essentially effective when the mean distance between impurity ions is much longer than the coherence length in the \( ab \)-plane [3]. However, impurity doping to the Cu in the CuO₂ plane always accompanies large decrease in \( T_c \). Therefore, dilute doping to the other cation sites are believed to be more effective for enhancement of \( J_c \) characteristics, because local lattice distortion responsible for slightly weaker superconducting region can be introduced by small amount of cation substitution. The locally introduced weak superconducting regions are expected to act as the pinning sites.

In the present study, we have attempted to improve \( J_c \) under magnetic fields for RE123 single crystals and melt-solidified bulks by low level chemical doping to various cation sites to create locally weak superconducting regions. In this report, recent results mainly on the Y123 will be shown.
2. Experimental

Single crystals and large bulks of doped Y123 were synthesized by the flux and melt-solidification methods, respectively, with nominal compositions of $Y(Ba_{1-x}Sr_x)_{2}Cu_3O_y$ ($x < 0.02$), $Y_2LaBa_2Cu_3O_y$ ($x < 0.01$) and $(Cu_{1-x}Co_x)Ba_2YCu_3O_y$ ($x < 0.03$). The single crystals were prepared by the flux method using BaZrO$_3$ crucibles. The Y123 melt-solidified bulks were prepared as follows; the calcined powder of $Y_2BaCuO_5$ (Y211) was mixed with the doped Y123 calcined powder with a molar ratio of 3:7, pressed into pellets with 20 mm in diameter and ~8 mm in thickness. The pellets were heated up to ~1030°C, kept for 1 h, and slowly cooled from 1010°C to ~994°C at a rate of 0.4°C/h in air. Nd123 single crystals were used for the seed crystals which were placed at the center of each pellet. For single crystals, oxygen annealing was performed at 400°C for 150 h and 450°C for 100 h for Sr-doped and Co-doped crystals, respectively. Oxygen annealing conditions for the melt-solidified bulks were 370°C for 200 h for Sr- or Lu-doped Y123 and 450°C for 100 h for Co-doped ones. Magnetic properties were investigated by a SQUID magnetometer under $H \parallel c$. $J_c$ was calculated from width of the magnetization hysteresis loops based on the extended bean model. In the magnetization measurements for the melt-solidified bulks, small rectangular samples with a typical dimension of 1 x 1 x 1 mm$^3$, which were cut from just under the seed crystal ~1 mm below it (c-growth region), were used.

3. Result and Discussion

3.1. Dilute doping effect of Sr to Ba site

In our previous study, the low level Sr doping ~0.2% for Ba site was found to be effective for enhancement of $J_c$ for the $a$-growth region of the Y123 melt-solidified bulks particularly under 1~2 T by development of the second peak effect. In the present study, we have confirmed that the dilute doping less than 0.5% of Sr to Ba enhance $J_c$ characteristics also in the c-growth region. In the case of the Sr-doped Y123 single crystals, dilute Sr doping of 0.05% to Ba exhibited the highest $J_c$ at 63 K, while 2% Sr-doped sample exhibited highest $J_c$ accompanying large second peak effect at 77 and 84 K as shown in Fig. 1, in spite of its slightly suppressed $T_c \sim 89$ K. The 0.05% and 0.5% Sr-doped samples maintained their peak effect at 77 K, however, they were less prominent compared with that of the 2% doped sample. Since the superconducting coherence length of Y123 is approximately 6 nm at 84 K, which is much longer than the mean distance between the Sr ions in the 2% Sr-doped sample (2.9 nm), inhomogeneous distribution of Sr ions is believed to contribute the second peak effect as in Pb-doped Bi2212 single crystals [4].

![Fig. 1. $J_c - H$ curves for Sr-doped Y123 single crystals at 77 K (a) and 84 K (b).](image-url)
3.2. Dilute doping effect of Co to Cu site in the Cu-O chain
In general, substitution of Co in RE123 is considered to be mainly for the Cu at the CuO-chain [5]. Therefore, the Co doping for RE123 does not accompany large decrease in $T_c$. In the present study, we confirmed that a high $T_c \sim 92$ K was maintained even for a 3 % Co-doped Y123 melt-solidified bulk with showing sharp superconducting transition in the temperature dependence of magnetization measurements under 1 Oe. Figure 2(a) and 2(b) show the $J_c - H$ characteristics for Co-doped Y123 single crystals and melt-solidified bulks, respectively, at 77 K.

![Fig. 2. $J_c - H$ curves at 77 K for Co doped Y123 single crystals (a) and melt-solidified bulks (b).](image)

A Co-free Y123 single crystal exhibited small second peak effect, which is probably originated from the existence of a certain amount of oxygen defects in the crystal which act as field-induced pinning sites [6]. The Co-doped single crystals exhibited apparently larger second peak effects and higher at $J_c$ below \sim 3 T. Similarly, the Co-doped Y123 melt-solidified bulks showed high $J_c$ performance. The nominal optimal doping levels of Co for $J_c$ characteristics were 0.5 % and 2 % for single crystals and melt-solidified bulks, respectively. This difference might be explained by presence of Y211 in the melt-solidified bulks, which can include a certain amount of Co.

3.3. Dilute doping effect of Lu to Y site
Since the Lu$^{3+}$ is the smallest ion among the rare-earth elements, local lattice shrinkage of the CuO$_2$-plane can be introduced by Lu doping to the Y site. Figure 3 shows the external field dependence of $J_c$ for Lu-doped Y123 melt-solidified bulks at 77 and 84 K. The dilute Lu doping less than 0.5 % for Y did not largely enhance the second peak effect of the Y123, however, $J_c$ under high magnetic fields was apparently improved and corresponding irreversibility fields were also enhanced. This result suggests that various combinations of rare earth elements having different ionic radii can improve high field $J_c$ performance of RE123 materials.

3.4. Discussions on the dilute doping effect for Y123 system
All the examined dilute doping, such as Sr to Ba, Lu to Y and Co for Cu at the CuO-chain, improved critical current properties of Y123 single crystals and/or melt-solidified bulks. These means that dilute impurity doping to the all the cation sites is effective for enhancement of flux pinning properties. It should be noted that the dilute doping attempted in the present study did not accompany large decrease in $T_c$. This is apparently advantageous point compared with the impurity doping to the CuO$_2$-plane, which always accompany serious decrease in $T_c$. In the cases of Sr doping for Ba and Lu doping for Y,
these doping do not change electronic state largely because of equivalent doping. Therefore, introduced local lattice distortion by doping of Sr or Lu is considered to be essential for enhanced $J_c$ under magnetic fields accompanying the second peak effect, which corresponds to the disorder transition of the vortex lattice induced by disorders in the crystal lattice.

On the contrary, the Co doping for Cu accompanies various changes, such as electron doping, structural change in the Cu-O chain, which may affect the chain structure, and slight enlargement of the $ab$-plane. Therefore, the essential effects of Co doping on the largely improved critical current properties were quite difficult to be understood at the present stage. Systematic studies on the transport properties and microstructural observation are undergoing for Co-doped Y123 single crystals to clarify the mechanisms of the improved $J_c$ by Co doping.

Fig. 3. $J_c - H$ curves at 77 and 84 K for Lu-doped Y123 melt-solidified bulks.

4. Conclusions
Dilute impurity doping to various cation sites in Y123 was attempted to improve flux pinning properties. All the low level doping, such as Sr to Ba, Lu to Y, Co to Cu in the Cu-O chain, resulted in enhancements of critical current properties. The Sr and Co doping accompanied large second peak effect, while the irreversibility fields were not improved. On the other hand, the Lu-doped Y123 exhibited improved irreversibility fields. These mean that the impurity doping effect can be tunable by selection of dopants and doped cation sites. In addition, co-doping technique may lead further improvement of $J_c$ characteristics for RE123 materials. The dilute doping technique will be extended for practical RE123 bulk magnets as well as the RE123 coated conductors.

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