Enhanced Flux Pinning Properties of RE123 Melt-Solidified Bulks by Dilute Impurity Doping

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Abstract. In our previous study, dilute impurity doping to various cation sites of the Y123, particularly to the Cu site in the Cu-O chain, was found to dramatically enhance $J_c$ of single crystals and its melt-solidified bulks. In order to clarify the essential role of dilute doping for improved pinning, TEM observation was performed for Co or Ga doped Y123 melt-solidified bulks. Density of twins did not change by the Co and Ga doping. The local compositional analysis by TEM-EDS indicated that the doped Co homogeneously dispersed in the Y123 matrix. These suggested generation of point-defect-like pinning centers by dilute doping for Cu site of the CuO chain. In addition, further enhancement of $J_c$ was attempted for Dy123 melt-solidified bulks by the same method. The Co-doped Dy123 melt-solidified bulks also exhibited improved $J_c$, particularly for samples grown under higher cooling rate during crystal growth. A high $J_c$ of $\sim 60 \text{ kA cm}^{-2}$ under $10-20 \text{ kOe}$ at $77 \text{ K}$ was achieved, when a cooling rate of 0.9°C/h was applied. Systematic decrease in $J_c$ with an increase of the cooling rate observed for undoped Dy123 bulks suggested that the high cooling rate suppressed partial Dy substitution for the Ba, resulting in a decrease of effective pinning sites. Therefore, the high $J_c$ observed for the Co-doped Dy123 bulk grown under a high cooling rate can be explained by generation of effective pinning sites around Co ions in the strong superconducting matrix of Dy123 with low substitution level of Dy at the Ba site.

1. Introduction
The REBa$_2$Cu$_3$O$_y$ (RE123, RE = rare earth elements) melt-solidified bulks are the most excellent materials as for bulk magnets generating high-magnetic fields using its high critical current density, $J_c$, under magnetic fields. Due to its high operating temperature, such as $77 \text{ K}$, low electric power consumption and high magnetic gradient, bulk materials are expected to replace present electric coils or permanent magnets. Several applications, such as magnetic separation systems, medical drug delivery systems (MDDS) and motors installed in marine vessels, etc. have been developed thus far. For these applications, improvement of the trapping fields is still required. Therefore, introduction of various flux pinning centers to RE123 melt-solidified bulks has been attempted for enhancement of $J_c$.

Finely dispersed RE$_2$BaCuO$_3$ (RE211) precipitates in RE123 matrix are well recognized as one of the effective flux pinning centers under low magnetic fields. In addition of refinement of these precipitates, introduction of other non-superconducting particles, such as BaSnO$_3$ [1], has also enhanced $J_c$ mainly under low magnetic fields. On the other hand, fine RE-rich RE123 clusters, which originate from inhomogeneous RE substitution for Ba, are well known to act as strong pinning centers.
under high magnetic fields [2]. Furthermore, low level Zn substitution for the Cu site in the CuO
plane was reported to be effective for enhancement of \( J_c \) of Y123 melt-solidified bulks [3]. Similar
effect was also reported for Ni doped Y123 melt-solidified bulks [4] and Co doped Bi(Pb)2212 single
crystals [5]. These results mean that dilute doping to the Cu site in CuO plane is universally effective
for the enhancement of \( J_c \) under magnetic fields. However, this method always accompanies large
suppression in \( T_c \) of the RE123 matrix, which must be a disadvantageous point for their wide range
applications particularly at high temperatures.

In our previous study, we discovered that dilute impurity doping to the selected cation site in the
RE123 lattice, especially to the Cu site in Cu-O chain, dramatically enhanced \( J_c \) of Y123 single
crystals and its melt-solidified bulks at 77 K [6]. In this paper, we discuss about the pinning
mechanisms of the small amount of impurity doped Y123 through microstructural observation by
transmission electron microscopy (TEM). In addition, we have attempted further enhancement of flux
pinning properties for Dy123 melt-solidified bulks by the same method, because Dy123 is believed to
be more promising materials than Y123 system in terms of \( T_c \) and critical current properties.

2. Experimental

High purity powders of RE\(_2\)O\(_3\), BaCO\(_3\), CuO, CoO\(_4\) and Ga\(_2\)O\(_3\) (99.9%) were used as raw materials
for Co or Ga-doped RE123 and RE211. The RE123 calcined powders with nominal compositions of
REBa\(_2\)Cu\(_{3-x}\)M\(_x\)O\(_y\) (RE = Y, Gd and Dy, M = Co and Ga; \( x = 0, 0.02 \) and 0.1) were prepared by heating
raw powder mixtures at 880°C for 24 h in air. Fine powder of RE211 was prepared by calcination at
800°C for 120 h in air. Obtained RE123 and RE211 powders were mixed with a molar ratio of 7:3,
and 0.5 wt% of Pt powder was added. This mixture was uniaxially pressed into a pellet with 20 mm in
diameter and \( \sim 8 \) mm in thickness. REBa\(_2\)Cu\(_{3-x}\)M\(_x\)O\(_y\) melt-solidified bulks were synthesized by the
cold-seeding method in air using Nd123 single crystals as seed crystals to obtain bulks with single
domain. Various cooling rate of 0.9~0.4°C h\(^{-1}\) was applied in the crystal growth process. Samples
with typical dimensions of \( \sim 1.7 \times 1.7 \times 0.7 \) (// c) mm\(^3\) were cut from the same part of bulks, 1 mm
below the seed crystal, for magnetization measurements and microstructural observations. Oxygen
annealing conditions were 450°C for 100 h for Y123 samples and 400°C for 120 h for Dy123 and
Gd123 samples. Superconducting properties were measured by a SQUID magnetometer (Quantum
Design MPMS-XL5s) under fields applied parallel to the c-axis. \( J_c \) was calculated from the width of
the magnetization hysteresis loop using the extended Bean model.

TEM observations were carried out for samples grown under a cooling rate of 0.8°C h\(^{-1}\) by zone
axis incidence with an accelerating voltage of 200 keV using JEOL 2000-EX and JEOL 2010-F
equipped with energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Microstructures of impurities doped Y123 melt-solidified bulks

RE123 melt-solidified bulks synthesized in the present study were composed of single domain. TEM
observation for undoped and Co or Ga doped (\( x = 0.02 \)) Y123 melt-solidified bulks revealed that all
the samples have similar twin structures with spacing of 100~300 nm. It was reported that several %
of impurities, such as Fe, Co and Ga, substituting for Cu in the CuO chain increased the twin boundary
densities, while Zn or Ni did not influence the twin spacing [7]. However, in our samples with a low
nominal impurity doping level of \( x = 0.02 \), the twin boundary density did not significantly change and
any distortions due to inhomogeneous dispersion of dopants were not observed. In the local
compositional analysis for Co doped Y123 sample with \( x = 0.1 \), Co was detected in the Y123 matrix
with almost nominal concentration independent of the analyzed position, indicating homogeneous
dispersion of Co in the Y123 matrix. Combining our previous results [6], it was confirmed that
effective point-defect-like pinning centers corresponding to the local lattice distortions were introduced by dilute doping by Co or Ga to the CuO chain of RE123.

3.2. Influence of Dy$^{3+}$ substitution on critical current density for impurities doped Dy123 melt-solidified bulks

Figure 1 shows the $J_c$-$H$ curves for DyBa$_2$Cu$_{3-x}$Co$_x$O$_y$ bulks prepared under various cooling rates in the crystal growth process. It was found that $J_c$ for dilute Co-doped Dy123 melt-solidified bulks with $x = 0.02$ systematically improved with an increase of cooling rate during crystallization. In particular, the Co-doped sample prepared under a high cooling rate of 0.9°C h$^{-1}$ exhibited large second peak and its $J_c$ reached ~60 kA cm$^{-2}$ under 10 ~ 20 kOe at 77 K. Similar improvement was also confirmed for Ga doped Dy123 bulks with $x = 0.02$. Since $J_c$ for undoped sample decreases when the cooling rate becomes higher, the largely improved $J_c$ for the Co-doped sample with a high cooling rate is not due to an increase of the other defects, such as oxygen vacancies.

Recently, it was reported that the second peak effect of Dy123 melt-solidified bulks was enhanced by preparing under flowing pure oxygen atmosphere. This indicates that small amount of Dy$^{3+}$ can incorporate to the Ba site [8]. Moreover, it has been pointed out that the slower cooling rate increases the substitution level of RE at the Ba site in a (Sm, Eu)123 melt-solidified bulk [9], whereas its mechanism has not been well understood yet. Figure 2 shows the bright-field TEM images of an undoped Dy123 samples grown under cooling rates of 0.8°C h$^{-1}$ (a) and 0.4°C h$^{-1}$ (b). On the contrary to the sample prepared under 0.8°C h$^{-1}$, the white and black contrast was observed in the sample prepared under 0.4°C h$^{-1}$. This contrast means the lattice distortion which is considered to correspond to the inhomogeneous chemical composition between Dy and Ba in Dy123. Therefore, this result suggests that crystallization under slow cooling rate promotes Dy incorporation to the Ba site.

Figure 3 shows the relationship between cooling rate and the maximum flux pinning force, $F_{p(max)}$, at 77 K for undoped and impurity doped Dy123 melt-solidified bulks. The $F_{p(max)}$'s for undoped Gd123 melt-solidified bulks were also plotted. $F_{p(max)}$ for undoped Dy123 and Gd123 samples decreased with increasing the cooling rate. It should be noted that Gd substitution for Ba occurs more or less when the Gd123 sample is synthesized in air. $T_c$'s for Gd123 samples were systematically increased from 92.5 K to 94.5 K with increasing cooling rate from 0.4°C h$^{-1}$ to 0.8°C h$^{-1}$ while $T_c$ was almost unchanged for undoped Dy123 samples. These results indicate that high cooling rate decreased effective pinning sites corresponding to partial Dy and Gd substitution for the Ba site, although the substitution level of Dy for Ba would be quite low.
On the other hand, $F_{p(\text{max})}$'s were significantly increased for both Co or Ga doped Dy123 samples by applying high cooling rate, while the $T_c$ did not changed with an increase of cooling rate. Since samples prepared under high cooling rate have less amount of Dy substitution for the Ba site, the improved $F_{p(\text{max})}$ observed for the impurity doped samples can be explained by the deep pinning potential around impurity ions in inherently strong superconducting matrix, stoichiometric Dy123. It is interesting that the dilute impurity doping to the CuO chain is more effective method for enhancement of flux pinning properties than partial substitution of Dy for Ba in Dy 123. Systematic studies on the transport properties are undergoing to clarify the more essential effect of dilute doping to the CuO chain on flux pinning properties of RE123 crystals.

**4. Conclusions**

Pinning mechanism of enhanced $J_c$ by dilute impurity doping for Cu site in the CuO chain was examined by TEM observation performed for undoped and Co or Ga doped Y123 melt-solidified bulks. Twin boundary density was not changed by low level impurity substitution for Cu in the CuO chain. EDS analysis revealed the homogeneous dispersion of Co ions in the Y123 matrix. These suggested that the dilute impurity doping to Cu in the CuO chain generated point-defect-like pinning centers around the impurity ions. In addition, further increase of $J_c$ for Co or Ga doped Dy123 melt-solidified bulks was achieved by applying high cooling rate, which suppressed Dy substitution for Ba. The strong superconducting matrix corresponding to the stoichiometric cation composition in Dy123 is believed to contribute to an increase of pinning potential around Co or Ga ions.

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**References**

[1] J. Shimoyama et al., Jpn. J. Appl. Phys. **29** (1990) L1999
[2] S. I. Yoo et al., Appl. Phys. Lett., **65** (1994) 633
[3] G. Krabbes et al., Physica C **330** (2000) 181
[4] L. Shlyk et al., Supercond. Sci. Technol. **18**, L10 (2005).
[5] M. Shigemori et al., Physica C **408-410**, 40 (2004).
[6] Y. Ishii et al., Appl. Phys. Lett. **89** (2006) 202514
[7] Y. Xu et al., Phyica C **169** (1990) 205
[8] T. Nakashima et al., CryoPrague 2006 Vol. 2 (2007) 109-112
[9] A. Hu et al., Appl. Phys. Lett., **78** (2001) 2539