Largely Improved $J_c$ at Low Temperatures Observed in Y123 Single Crystals with Chemically Introduced Point Defects

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Abstract. Most of studies on pinning properties and relating vortex nature of the RE123 system were performed at high temperatures around 77 K. However, the pinning characteristics of RE123 at low temperatures have not been well understood yet, while extensive applications using the cryocooling system are also strongly expected. In the present study, the $J_c$-$H$-$T$ properties have been studied for Gd123 single crystal with a low level Gd substitution for Ba and Y123 single crystals substituted by small amount of impurity ions, such as Sr and Co, which improve $J_c$ properties accompanying huge peak effect in their $J_c$-$H$ curves. It was found that the increase in $F_p$ with decreasing temperature of the impurity doped Y123 samples were much larger than that of the Gd123 sample, while the Gd123 sample exhibited higher $J_c$ than these Y123 samples above 77 K. The $J_c$ performance below 50 K of the Gd123 sample was even lower than that of the undoped Y123 sample. This result strongly indicates that the RE123 with RE/Ba substitution does not appropriate for low temperature applications, such as high field magnets despite their good $J_c$ performance at high temperatures e.g. 77 K.

1. Introduction

Remarkable progress in the refrigeration technologies provides the possibility to RE123 superconducting materials to be used at lower temperatures than the liquid nitrogen temperature. Extraordinarily high trapping fields of 17 T for Y123 melt-solidified bulks (26 mmø) have been achieved at 29 K by use of the cryocooling systems [1]. In the case of power industry or the high field magnets using superconducting coils, the world record of 33.6 T has been achieved by SuperPower Inc. as a prototype operating at 4.2 K using RE123 coated conductors. For such applications, the maintenance-free cryocooler systems are more expected than using cryogen. Therefore it will be indispensable to characterize the critical current performances under magnetic fields for RE123 materials at temperatures below 77 K hereafter as well as understanding the $J_c$-$T$ behavior.

The lower temperature results in the higher $J_c$ because of the increase in the condensation energy of superconductors. From the viewpoint of the flux creep theory [2], it can successfully explain the temperature dependence of $J_c$ for RE123. However, the difference in the flux pinning
characteristics of the various point-defect-type pinning sites, such as RE/Ba substitution and oxygen deficiencies, have not been discussed explicitly, although RE123 materials always include such the pinning sites. Furthermore, our previous studies revealed that the chemical composition for Bi2212 single crystal considerably affect both on \( J_c \) and \( H_{\text{irr}} \). These mean that those properties for RE123 may be influenced by its cation stoichiometry as well, although it has not been well discussed thus far except for RE123 with light RE elements, such as La, Nd, Sm, Eu and Gd.

In this paper, we compared the \( J_c-H \) properties for the Y123 and Gd123 single crystals. Y123 single crystals with newly discovered point-defect-type pinning sites [5], which were introduced by substituting impurity ions with low concentration to the specific sites, are also examined. According to the transmission electron microscope study, it was revealed that these substituted ions did not form the large clusters such as RE/Ba substitutions [6, 7], suggesting that the volume of pinning sites by these impurities is much smaller than that of the RE-rich local regions with typical size of several ten nm as reported several literatures. Their \( J_c-H-T \) properties were discussed from the viewpoint of the difference in the spatial size of these pinning sites.

2. Experimental

The undoped, Sr-doped and Co-doped Y123 single crystals and the undoped Gd123 single crystal were grown by the self-flux method in air using high quality BaZrO\(_3\) crucibles. For Y123 single crystals, starting compositions of the flux were Y : Ba : Sr : Cu = 1 : 29.6 : 0.6 : 68.8 (in molar ratio) and Y : Ba : Cu : Co = 1 : 30 : 60 : 0.3, which correspond to 2 mol% Sr-doping for barium and 0.5 mol% Co-doping for copper in CuO chain, respectively. Details of the synthesis procedure will be found in ref. [5]. The Gd123 single crystals were grown in air from flux powder with a composition of Gd : Ba : Cu = 1 : 20 : 30 by following temperature pattern. The flux in a BaZrO\(_3\) crucible was heated up to 1070\(^\circ\)C, kept for 3 h, and then slowly cooled from 1030 to 980\(^\circ\)C at a rate of 1.67\(^\circ\)C h\(^{-1}\). After the decantation at 980\(^\circ\)C, Gd123 single crystals were slowly cooled down to room temperature in the furnace. The typical size of the obtained single crystals were approximately 1 \( \times \) 1 \( \times \) 0.2 \( \sim \) 0.4//\( c \) mm.

Oxygen content for the crystals were increased by post-annealing in flowing oxygen as much as possible in order to eliminate the contribution from the oxygen deficiencies to the flux pinning by the stepwise changing of the annealing temperature from higher to lower; from 500\(^\circ\)C to 375\(^\circ\)C for the Y123, and from 400\(^\circ\)C to 300\(^\circ\)C for the Gd123. Superconducting properties were characterized by a SQUID magnetometer (Quantum Design MPMS-XL5s) under \( H//c \). The extended Bean model was used for calculation of \( J_c \) from the width of magnetization hystereses.

3. Results and discussion

The \( T_c \) onsets for the undoped, the Sr-doped and the Co-doped Y123 single crystals and the undoped Gd123 single crystal after annealing at each final annealing temperature were 91.9, 90.6, 91.6 and 93.3 K, respectively. Figure 1 shows the \( J_c-H \) curves measured at 40 K and 77 K for these single crystals. With respect to the contribution from the oxygen deficiencies to the peak effect in these \( J_c-H \) curves, it is considered to be almost eliminated by following reasons: systematic suppression of these second peaks were observed at 77 K for each crystals through the stepwise decrease in the annealing temperature, as was reported by Zhukov et al. [8]. Only small second peak was observed in the \( J_c-H \) at 77 K for the undoped Y123 sample in Figure 1, indicating that it includes very few effective pinning sites due to oxygen deficiencies, as well as for the other crystals. On the other hand, larger second peaks were observed for the impurity doped Y123 and Gd123 samples even after the almost fully oxygenation, meaning that the doped impurities and Gd/Ba substituted region certainly act as pinning sites and enhance \( J_c \) in magnetic fields.
Comparing their \( J_c - H \) properties at 40 K, it was found that the Gd123 sample exhibited the lowest \( J_c \) among these crystals although it exhibited high \( J_c \) at 77 K. For the Sr-doped and the Co-doped Y123 samples, the \( J_c - H \) properties at 40 K were better than that for the undoped Y123 single crystal due to additional pinning sites corresponding to the substituted impurity ions. Furthermore, the \( J_c \) for the undoped Gd123 single crystal immediately decreased with increasing magnetic fields, while the \( J_c \) for the undoped, Sr-doped and Co-doped Y123 single crystals were enhanced with increasing magnetic field at the same temperature. This indicates that pinning force of the Gd/Ba substituted regions is not large at low temperatures.

Figure 2 shows the \( F_p - T \) plots for these four crystals in 30 kOe calculated from the \( J_c \) at various temperatures. As seen in this figure, the temperature dependences of \( F_p \) were clearly different between Y123 and Gd123 crystals; The Gd123 single crystal exhibited the lowest \( F_p \) below 50 K among these samples although its \( F_p \) was highest above 77 K. This tendency was also observed in 10 kOe and 20 kOe. The inset in Fig. 2 shows the temperature dependence of normalized \( F_p \) by \( F_p(77 \text{ K}) \) in 30 kOe. Much larger increase in \( F_p \) for the Y123 samples were recognized than that for the Gd123 sample. This low \( F_p \) for the Gd123 sample strongly indicates that RE123 with high critical current properties at high temperature near \( T_c \) does not necessarily exhibit high \( J_c \) performance at lower temperatures. According to these results, the RE123 without RE/Ba solid solution is more suitable as a substance for the coated conductors aimed for low temperature applications.

Since this weak temperature dependence of \( F_p \) for the Gd123 sample did not depend on the magnitude of field except for low fields below 10 kOe, where twins also contribute for pinning due to the matching effect [9], the main reason for this difference is considered to be the different temperature dependence of the elementary pinning force \( f_p \) of these individual pinning sites. If the decrease in the pinning potential, \( U_p \), of the Gd123 matrix is the main reason, the \( F_p \) should decrease in whole magnetic fields and temperatures, not only the low temperature range. Therefore the temperature dependence of the \( f_p \) for these pinning sites were considered from viewpoint of the different spatial size.
Since the Gd/Ba substituted region has the typical size of several ten nm in the ab-plane [6, 7], which is much larger than the coherence length, $\xi_{ab}$, the difference in the condensation energy between the superconducting matrix and the Gd/Ba substituted region should give the pinning energy. Thus the $f_p$ for Gd/Ba substituted region is expressed in the framework of textbooks; $f_p,_{\text{Gd/Ba}} \approx \frac{\Delta B^2(t)}{4\pi n_0} \cdot \frac{\pi \xi_{ab}(td)}{2}$, where $t$ and $d$ represent $T/T_c$ and the length along c-axis of the Gd/Ba substituted region, respectively.

On the other hand, it is unclear how the doped impurity ions affect the pinning energy, although there are possible two mechanisms; one is the difference in the condensation energy due to normal conducting or weak superconducting region around the impurity ion, and another is the decrease in the coherence length by the defect [10] due to the scattering of superconducting electrons by impurity ions and/or lattice deformation around them. Useful and basic method is provided by Thuneberg et al. [11]. Here we make a qualitative explanation for this case by considering each mechanism. When considering the former one, we have to define the phase boundary between the superconducting matrix and the normal conducting (or weak superconducting) region assuming that the regions around the impurity ions act as a normal conducting (or weak superconducting) pinning site. However, the actual phase boundary cannot be distinguished. Therefore the effective size of the pinning site with sphere shape was considered where the superconductivity would almost disappear or weaken. Since the superconducting order parameter changes in the vortex, the most stable configuration is that the centerline of the vortex penetrates the center of this small pinning site. Therefore the pinning energy will vary in a distance of approximately $\xi_{ab}$. This means that the $f_p$ will increase more with decreasing $\xi_{ab}$ than that of Gd/Ba substituted region since $f_p = (\delta U_p/\delta r)_{\text{max}} (\delta r \approx \xi_{ab})$, where $r$ is the distance between the vortex center and the pinning site. For the latter case, the gradient of the superconducting order parameter $|\partial \Psi|^2$ was given by equation (3) in ref. [12] according to Kes. It can be derived from the eq.(3) that the maximum value of the $\frac{d|\partial \Psi(r)|^2}{dr}$ ($\propto f_p$) is given at $r = \xi_{(\text{matrix})}$. In other word, the spatial change in the pinning energy is approximated more simply by $\xi_{ab}$ as well. This leads that $f_p$ will also largely increase with decreasing temperature. Therefore the temperature dependence of the impurity ion comes to be roughly $1/\xi_{ab}^2$ times larger than that of Gd/Ba substituted region according to all these estimation. They qualitatively agree with the observed $F_p$-$T$ tendencies.

Regarding the significant increase in $J_c$ for the undoped Y123 sample compared to the Gd123 sample, there is a possibility that the almost stoichiometric cation composition of Y123 increases $J_c$ as in the case of Bi2212 [3]. Further characterizations are needed such as $J_c$ at high field near the irreversibility field.

4. Conclusions
We have studied the $F_p$-$T$ properties for the undoped and impurity substituted Y123 and undoped Gd123 single crystals. Large temperature dependence of $F_p$ was observed for the Sr- and Co-doped Y123 single crystals compared to that for the Gd123 single crystal. These temperature dependences agreed well with estimated $f_p$-$t$ tendencies, indicating that the $f_p$ properties of point-defect-type pinning sites also largely affect the macroscopic critical current performance even if their absolute values are very small. In addition, these results indicate that the RE123 with RE/Ba substitution is not the appropriate substance for the low temperature applications.

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