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Effect of element substitution on the superconducting properties of Gd-based melt-processed bulk-superconductors

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Abstract. We studied the effect of Co doping on the superconducting properties of melt-processed Gd-Ba-Cu-O bulk-superconductors and compared the results with Zn doping, the former substitutes for Cu of the Cu-O chain while the latter to the CuO$_2$ plane. The critical current density ($J_c$) at 77 K of the region beneath the seed crystal increased with the Co$_3$O$_4$ content up to 0.23 wt.%, and that of the $a$-growth region about 5 mm away from the seed crystal up to 0.30 wt.%. The analysis of the pinning force showed that Co doping increases the amount of normal pins ($\delta l_{\text{pinning}}$). The measurements of the time dependence of the trapped field of the samples doped with various amounts of Co$_3$O$_4$ indicated that the creep rate at 77 K increases with Co$_3$O$_4$ content. This result suggests that the pinning potential of the normal pin created by the addition of Co$_3$O$_4$ is relatively small.

1. Introduction
Since the report that adding a small amount of ZnO enhances $J_c$ and the trapped field ($B_T$) of melt-processed YBa$_2$Cu$_3$O$_y$ bulk superconductors [1], diligent efforts have been devoted to improve the properties of bulk superconductors by adding impurities that substitute for Cu of the CuO$_2$ plane [2-7]. These studies consistently showed that $J_c$ and the trapped field can be increased with a proper amount of doping of this type of impurities. However, this type of impurities decreases largely the superconducting transition temperature ($T_c$). Therefore, the optimal Zn content that maximizes $B_T$ is very small and adding an excess amount of Zn more than the optimal content rather suppresses $J_c$. On the other hand, there are many other elements that substitute to a site other than Cu of the CuO$_2$ plane. The decrease of $T_c$ is generally more gradual with such impurities. Co is one of such elements and substitutes for Cu of the CuO chain. In a preceding work, we have studied the effect of doping Co and found that $J_c$ and $B_T$ at 77 K increase without a noticeable decrease in $T_c$ at least when the amount of the added Co$_3$O$_4$ was small (ca. 0.20 wt.%) [8]. Since the decrease in $T_c$ is relatively small, the optimal content of Co$_3$O$_4$ that maximizes $B_T$ was 0.23 wt.%, which is larger than that of ZnO, 0.10 wt.% [9].

In the present work, we further studied in detail the effect of Co doping and varied the Co$_3$O$_4$ content for a wider range. We systematically studied $T_c$, $J_c$ and the creep of trapped field for samples containing various amounts of Co$_3$O$_4$. The trapped field of the 0.30 wt.% Co$_3$O$_4$ added sample exceeded that of the non-doped one by 23% when measured immediately after the external field was turned off, reflecting the increase of $J_c$. Despite the increase of $J_c$, however, the creep rate of $B_T$ increased with the Co$_3$O$_4$ content. Taking into account the results of pinning force analysis, we think that the pinning potential of the normal pin ($\delta l_{\text{pinning}}$) created by doping Co$_3$O$_4$ is relatively small,
and this caused the increase of the creep rate of the trapped field at 77 K with increasing the Co$_3$O$_4$ content.

2. Experimental details

The Gd-Ba-Cu-O bulk superconductors were prepared by a melt process. Commercially available powders of the GdBa$_2$Cu$_3$O$_y$ (Gd123) and Gd$_3$BaCuO$_5$ (Gd211) phases were mixed in a molar ratio of Gd123:Gd211 = 5:2, and 15 wt.% Ag$_2$O was added to improve the mechanical strength of the sample. 0.5 wt.% Pt to refine the Gd211 precipitates. Zn- or Co-doped samples were prepared by adding various amounts of ZnO or Co$_3$O$_4$ to these starting powders. The contents of ZnO and Co$_3$O$_4$ are described as a percentage of the weight sum of the Gd123 and Gd211 powders throughout this paper rather than by the atomic ratio. This is because probably not all Zn or Co were taken into the Gd123 phase and the actual atomic composition of the superconducting phase would be different from the nominal one. To be able to compare our results with the data published by other groups however, it would be nevertheless worthwhile to point out that if all additive atoms substituted for the atoms of the Gd123 phase, adding 0.10 wt.% of ZnO corresponds to replacing 0.398% of Cu to Zn, and 0.10 wt.% of Co$_3$O$_4$ corresponds to replacing 0.404% of Cu to Co. The melt-process was performed in a 1% O$_2$ / 99% Ar atmosphere. After finishing the growth process, the sample was heated to 400 °C, and then slow cooled to 300 °C in 350 h under flowing pure oxygen gas. The obtained bulk superconductors were 30 mm in diameter. The time dependence of the trapped field was measured using a Gifford-McMahon cycle refrigerator to cool the sample and a transverse-type Hall sensor (F. W. Bell, model BHT 921) that was mounted on the center of the sample's top surface. The sample was field-cooled from 100 K to 77 K under 3 T.

To study the local superconducting properties, we measured magnetization of small specimens that were cut from the bulk samples using a SQUID magnetometer (Quantum Design, MPMS-7) by applying the external field parallel to the c-axis. The $J_c$ values were estimated from the magnetic hysteresis loop widths according to the extended Bean model [10]. The irreversibility field ($B_{irr}$) was determined from the field dependence of $J_c$ with a criterion of $J_c = 50$ A/cm$^2$.

3. Results and discussion

We measured the local superconducting properties on small samples that were cut from the bulk superconductors. The locations from where the small specimens were taken are shown schematically in Fig. 1a. Figure 1b shows the temperature dependence of magnetization of the specimens that were cut from position C (a-growth region about 5 mm from the seed crystal), and Fig. 1c summarizes the impurity content dependence of the onset $T_c$ for positions A (the region beneath the seed crystal),
C and E (a-growth region about 10 mm from the seed crystal). It can be seen that $T_c$ did not show a significant change with adding Co$_3$O$_4$ up to 0.40 wt.%. This is in a strong contrast to the case of ZnO doping, which strongly depressed $T_c$ as is also shown in Fig. 1c. With further increasing the Co$_3$O$_4$ content to 0.60 wt.%, $T_c$ suddenly started to decrease. Aoki et al. reported that when the ratio of Co to Cu exceeded $x_c = 1.7\% \sim 3\%$, an orthorhombic to tetragonal transition took place and $T_c$ started to decrease within a nearly linear Co content ($x$) dependence of $dT_c/dx = -600$ K/Co ion per Cu site [11]. In the present study, $T_c$ started to decrease at Co$_3$O$_4$ content of about 0.40 wt.%. This corresponds to about 1.6 atom.% if we assume that all Co were taken into the superconducting phase, which is close to the critical content $x_c$ reported by Aoki et al. It seems therefore that a large fraction of the added Co atoms substituted for Cu of the superconducting phase. Figure 1c indicates that $T_c$ has no significant position dependence at least at low Co$_3$O$_4$ concentration up to 0.30 wt.%. 

Figures 2a and b show the field dependence of $J_c$ at 77 K of positions A and C of the Co$_3$O$_4$ added samples. For comparison, $J_c$ of the optimal content (0.10 wt.%) ZnO sample is also included in the figures. By adding Co$_3$O$_4$, $J_c$ increased at both positions for a wide field range and the enhancement of $J_c$ was particularly large at position A. The largest $J_c$ at position A was observed with 0.23 wt.% Co$_3$O$_4$ doping, and the optimal content was 0.30 wt.% at position C. On the other hand, $J_c$ at both positions increased rapidly when the Co$_3$O$_4$ content was increased to 0.60 wt.%. This reduction of $J_c$ can be attributed to the large decrease of $T_c$. The irreversibility field ($B_{irr}$) and the field position of the secondary peak ($B_p$) decreased systematically to lower fields with the Co$_3$O$_4$ content.

Figure 3 summarizes $B_{irr}$ and $B_p$ of positions A, C and E of the samples with various amounts of

![Figure 2](image_url)  
**Figure 2.** The field dependence of $J_c$ of Co$_3$O$_4$ added Gd-based bulk superconductors measured at 77 K. For comparison, $J_c$ of 0.10 wt.% ZnO doped sample is also included. (a) The region beneath the seed crystal (position A) and (b) the a-growth region about 5 mm away from the seed crystal (position C).

![Figure 3](image_url)  
**Figure 3.** Summary of $B_{irr}$ and $B_p$ for various Co$_3$O$_4$ contents at positions A, C and E together with the data of samples containing various amounts of ZnO. The solid lines are guides for eyes.
Co$_3$O$_4$. Data of $B_{irr}$ and $B_p$ for various amounts of ZnO added samples are also plotted for comparison. Obviously, $B_{irr}$ and $B_p$ showed a systematic decrease with Co$_3$O$_4$ and ZnO content. However, the decrease of $B_{irr}$ and $B_p$ with impurity content is less significant for Co$_3$O$_4$ doping. Figure 3 also indicates that $B_{irr}$ and $B_p$ are roughly position independent. These data, together with the weak position dependence of $T_c$ mentioned above, suggest that the doped Co atoms are distributed homogeneously throughout the bulk sample at least when the Co$_3$O$_4$ content is small.

Figure 4a shows the field dependence of the pinning force ($F_p(B) = J_r(B)$) of the Co$_3$O$_4$ doped samples, and Fig. 4b the $B/B_{irr}$ dependence of the normalized volume pinning force ($F_p/F_{p,max}$). As shown in Fig. 4b, the peak positions of the normalized pinning force are relatively high for samples with low Co$_3$O$_4$ content and are close to $B/B_{irr} = 0.50$. This is the value predicted theoretically for the so-called $\delta T_c$ pinning [12]. In the non-doped sample, an up-shifted shoulder appeared in the $F_p/F_{p,max}$ curve in the field range of $B/B_{irr} < 0.2$. This may indicate that both normal pinning ($\delta T_c$ pinning) and $\delta T_c$ pinning were strong in this system [13,14]. The peak of the $F_p/F_{p,max}$ curve located at the highest $B/B_{irr}$ value when 0.10 wt.% Co$_3$O$_4$ was added, and decreased systematically from $B/B_{irr} = 0.49$ to 0.38 with increasing the content of Co$_3$O$_4$ from 0.10 to 0.40 wt.%. This indicates that adding Co$_3$O$_4$ beyond 0.10 wt.% increases dominantly the fraction of normal pins.

Figure 5a shows the time dependence of the trapped field ($B_r(t)$) of the Co$_3$O$_4$ doped samples at 77 K, and Fig. 5b the same data normalized by $B_r$ recorded immediately after the external field was swept down to zero ($B_r(0)$). As shown in Fig. 5b, the flux creep rate at 77 K increased with Co$_3$O$_4$ content. This is rather unexpected because $J_r$ increased up to 0.23 wt.% Co$_3$O$_4$ at position A and up to 0.30 wt.% Co$_3$O$_4$ at position C. We think that the unexpected increase in the creep rate is because the pinning potential of the pinning sites that were created by adding Co$_3$O$_4$ and the already existing pins is different. The analysis of the pinning force suggests that doping Co is more effective in increasing the number of normal pins relative to $\delta T_c$ pins. Therefore, the results of Fig. 5b probably imply that the
normal pin created by adding Co₃O₄ has a lower pinning potential in comparison to the already existing pins. Namely, the number of normal pins increases with Co₃O₄ doping and therefore \( J_c \) increases, but the pinning potential of the normal pin created by Co-doping is small, and the effective pinning potential decreases in average. As a result, the creep rate of the trapped field increased with the Co₃O₄ content. Furthermore, the trapped field of the 0.30 wt.% Co₃O₄ doped sample became smaller than that of the 0.10 wt.% doped sample within the time window of Fig. 5a. This is consistent with our earlier report of the trapped field distribution at 77 K [9], which showed that \( B_T \) measured after finishing the mapping of the field distribution, which corresponds to the trapped field about 20-30 min after switching off the external field, was larger for the 0.10 wt.% Co₃O₄ doped sample than the 0.30 wt.% doped one.

4. Conclusions
We have systematically studied the effect of doping Co to Gd-Ba-Cu-O melt-processed bulk-superconductors and compared the results with the effect of Zn doping. The measurements of small samples that were cut from the bulk superconductors showed that the optimal content of Co₃O₄ for increasing \( J_c \) was 0.23 to 0.30 wt.%. We also found that by doping Co, the irreversibility field and the secondary peak field at 77 K decreased systematically to lower fields. However, the decrement of \( B_{irr} \) and \( B_p \) was less significant compared to ZnO doping. We also estimated the pinning force and found that the influence of normal pin increases with Co₃O₄ content. The creep measurements of the trapped field showed that the creep rate increases with Co doping, although \( J_c \) increases up to 0.23 to 0.30 wt.% Co₃O₄. This result suggests that the normal pin created by adding Co₃O₄ has relatively lower pinning potential compared to the already existing pins and the effective pinning potential decreases in average with Co doping.

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