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The effect of Ca doping on the properties of melt-processed Gd-based bulk superconductors

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ABSTRACT

The effect of Ca doping to melt-processed Gd-based bulk superconductors fabricated by the oxygen-controlled melt growth (OCMG) method was studied. First, we simply added $CaCO_3$ to the starting materials to dope Ca and observed an increase in the trapped field and the critical current density (J_c) up to, at least, 0.31 wt.% $CaCO_3$. However, an additional oxygen annealing resulted in a decrease of J_c in magnetic fields and in a monotonous exponential-like field dependence of J_c. This suggests that oxygen deficiency had caused the enhancement of J_c, although the same annealing process as the non-doped sample was applied. We also prepared samples by adding not only $CaCO_3$ but also $BaCO_3$ and CuO in a molar ratio of Ca:Ba:Cu = 1:2:3, and observed a large peak effect of J_c up to at least 0.31 wt.% $CaCO_3$. It is likely that this large peak effect is also caused by oxygen defects, although the superconducting transition temperature was significantly large. These results indicate that J_c at 77 K can be significantly enhanced by introducing a proper amount of oxygen deficiency and compensating at the same time the decrease of carrier density by Ca doping.

1. Introduction

Since *c*-axis oriented single-grain $REBa_2Cu_3O_y$ (RE = Y, Nd, Sm, Eu, Gd, Dy, etc.) bulk superconductors prepared by melt-processing have an ability of trapping a large amount of magnetic flux when they are cooled under a magnetic field, they can be used as compact and strong quasi-permanent magnets when combined with a refrigerator [1]. Increasing the critical current density (J_c) is crucially important for further expanding the area these materials can be used, because the trapped field of a bulk superconductor depends on J_c. Therefore, diligent efforts have been made to improve J_c by, for instance, changing the RE element [2–7], reducing the size of pinning centers [5,8], irradiation [9,10], introducing nanocomposites [11], chemical doping [12–23] and so on.

On the other hand, the substitution of Ca for RE increases hole doping, which in turn decreases the anisotropy, and influences the superconducting transition temperature (T_c), J_c and the irreversibility field (B_{irr}) [24,25]. A study on magnetically aligned polycrystalline $(Y,Ca)Ba_2Cu_3O_y$ samples indicated that J_c at 0.2 T of a slightly overdoped sample was larger than that of optimally doped or underdoped samples [26]. The effect of Ca doping on melt-processed bulk superconductors was reported by Dalorme et al. [27] and Shlyk et al. [28], and J_c of their fully oxygenated Y–Ba–Cu–O samples decreased exponentially with the magnetic field. On the other hand, there is also a study reporting an observation of a peak effect in J_c for Ca-doped Y–Ba–Cu–O bulk superconductors, although Ce^{4+} was co-doped to compensate the change in hole doping [29]. Hence, the behavior of J_c when Ca is doped is conflicting. In the present work, we systematically studied the effect of doping Ca-to-Gd-based bulk superconductors. We observed a peak effect of J_c that can be attributed to oxygen deficiency, and the results suggest that if the decrease in carrier density is compensated by Ca doping, introducing a proper amount of oxygen defects can significantly enhance J_c at 77 K.

2. Experimental

The Gd–Ba–Cu–O (GdBCO) bulk superconductors were prepared by melt processing using the oxygen-controlled melt growth (OCMG) method. The non-doped samples were prepared by mixing commercially available powders of the $GdBa_2Cu_3O_y$ (Gd123) and Gd_2BaCuO_5 (Gd211) phases in a molar ratio of Gd123:Gd211 = 5:2, and 15 wt.% Ag_2O and 0.5 wt.% Pt. Ca-doped samples were prepared by adding various amounts of $CaCO_3$ to these starting powders. The content of $CaCO_3$ is described as a percentage of the weight sum of the Gd123 and Gd211 powders throughout this paper. If all additive Ca atoms would substitute for Gd of the Gd123 phase, adding 0.10 wt.% $CaCO_3$ corresponds to a substitution of 0.972% of Gd by Ca. The melt-process was performed in a 1% O_2/99% Ar atmosphere and the samples were grown by slowly cooling for 72 h with a cooling

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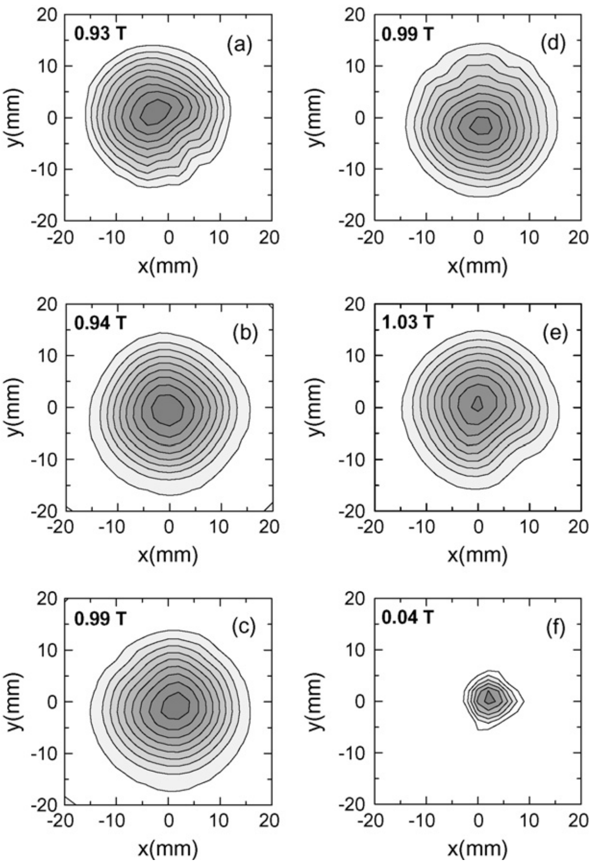

Fig. 1. Contour plots of trapped magnetic flux density of (a) non-doped, (b) 0.02 wt.%, (c) 0.10 wt.%, (d) 0.17 wt.%, (e) 0.31 wt.% and (f) 0.62 wt.% non-stoichiometrically $CaCO_3$ added samples measured at liquid nitrogen temperatures. The maximum trapped field of each sample is indicated at the upper left corner of each figure.

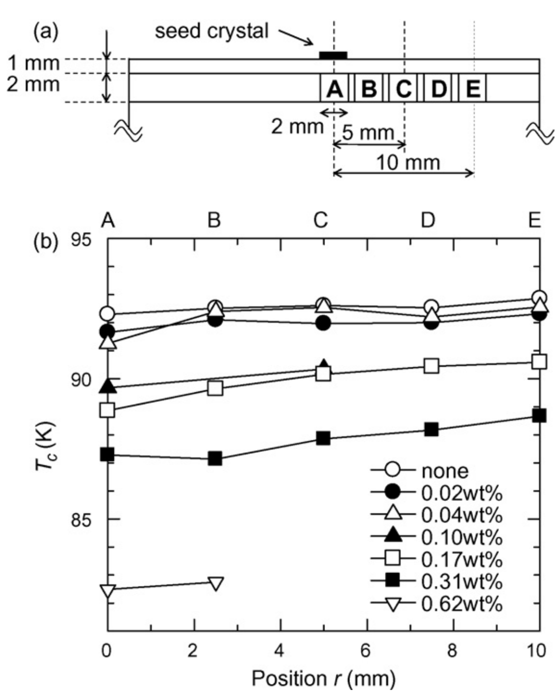

Fig. 2. (a) A schematic drawing of the locations from where the small specimens for magnetization measurements were taken from the bulk superconductor. (b) The position dependence of T_c of the non-stoichiometrically Ca-doped Gd–Ba–Cu–O bulk superconductors with various amounts of $CaCO_3$.

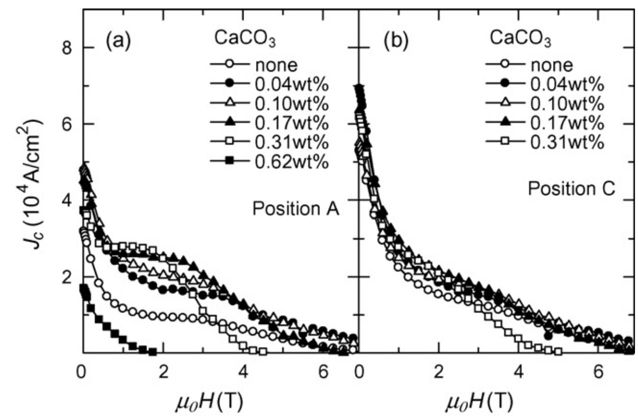

Fig. 3. The field dependence of J_c at 77 K of non-stoichiometrically $CaCO_3$ added samples measured after the same oxygenation process as a non-doped sample was applied; (a) the region beneath the seed crystal (position A) and (b) the *a*-growth region about 5 mm away from the seed crystal (position C).

rate of 0.50 °C/h. After finishing the growth process, the samples were heated to 400 °C, and then slowly cooled to 300 °C in 350 h under flowing pure oxygen gas. The obtained bulk superconductors were 30 mm in diameter. The trapped magnetic flux density was mapped using an axial-type Hall sensor (FWBell, model BHA 921), which was scanned 0.5 mm above the sample surface. The maximum trapped field values were measured by lowering the Hall sensor until it touched the sample surface. To study the local superconducting properties, we measured magnetization using a SQUID magnetometer (Quantum Design, MPMS-7) of small specimens that were cut from the bulk samples. The external field was applied parallel to the *c*-axis.

We also prepared bulk superconductors to which not only $CaCO_3$ but also $BaCO_3$ and CuO were added. The amount of these additive powders were adjusted so the atomic ratio of Ca, Ba, and Cu was Ca:Ba:Cu = 1:2:3. These samples are referred to as stoichiometrically doped samples, while we will refer to the samples described in the preceding paragraph as non-stoichiometrically doped samples. The cooling rate of the growth process of the stoichiometrically doped samples was the same as the non-stoichiometric samples, 0.50 °C/h, when the $CaCO_3$ content was 0.15 wt.% and 0.31 wt.%. When a larger amount of $CaCO_3$ was added, however, the growth rate was significantly lower, and we had to reduce the cooling rate. A 0.62 wt.% $CaCO_3$-doped sample was grown by slow cooling with a cooling rate of 0.17 °C/h for 36 h and then with a cooling rate of 0.40 °C/h for 40 h.

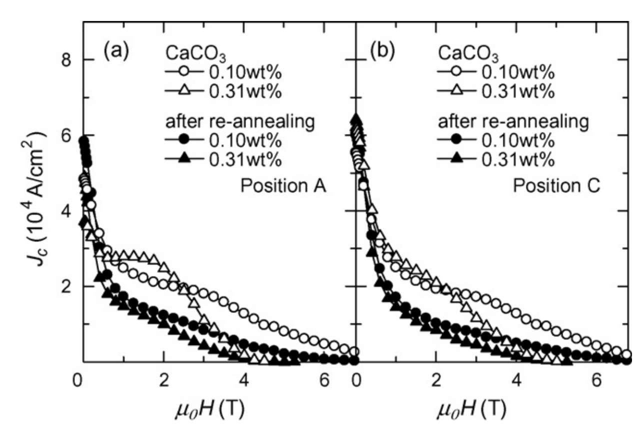

Fig. 4. The field dependence of J_c at 77 K of non-stoichiometrically $CaCO_3$ added samples measured after an additional heat treatment at 300 °C for 20 h together with the data before re-annealing shown in Fig. 3; (a) position A and (b) position C.