Effect of lanthanum addition on the fabrication of REBa$_2$Cu$_3$O$_y$ (RE=Gd, Sm and Dy) thin films by metal organic deposition using fluorine-free solutions

S Kato$^1$, R Kita$^1$, N Kobayashi$^2$ and O Miura$^2$

$^1$Shizuoka University, Johoku 3-5-1, Hamamatsu, Shizuoka 432-8561, Japan

$^2$Tokyo Metropolitan University, Minamiosawa 1-1, Hachioji, Tokyo 192-0364, Japan

E-mail: kita.ryusuke@shizuoka.ac.jp

Abstract. The effects of lanthanum (La) additions of 0.5–10 mol% on the superconducting properties and crystal growth of REBa$_2$Cu$_3$O$_y$ (REBCO, RE = Gd, Sm, and Dy) films fabricated by the fluorine-free metal-organic deposition method using 2-ethylhexanate solutions were investigated. La-doped REBCO films showed the decrease in the number density of holes on the film surface and the increase in the XRD peak intensity of the REBCO superconducting phases. La-added GdBCO with La contents of 0.5–3 mol%, and SmBCO and DyBCO films with La contents of 0.5–10 mol% showed improved critical current density ($J_c$) at the self-magnetic field compared to the pure films. For the GdBCO film, the $J_c$ value at the self-magnetic field increased from 1.32 to 2.38 MA/cm$^2$ upon La addition.

1. Introduction

REBa$_2$Cu$_3$O$_y$ (RE = Y and other rare earth elements) superconducting thin films are promising materials for high-temperature superconducting wires because of their high critical current densities ($J_c$’s) under large magnetic fields. Metal-organic deposition (MOD) is a suitable technique for mass production of REBCO thin films because it involves a non-vacuum and cost-effective process. Furthermore, the MOD process using fluorine-free solutions (FF-MOD), i.e., the process employed in the present study, is relatively simple since it requires no water vapor for removing fluorine from the films, unlike MOD using trifluoroacetates (TFA-MOD).

The development of REBCO films with superior high $J_c$ in magnetic fields ($B$) is essential for applications such as strong magnetic field generating coils and superconducting cables. Recently, the introduction of artificial pinning centers (APC) into REBCO films has been studied intensively, with the goal of enhancing $J_c$-$B$ performance [1-3]. In particular, REBCO films with Ba oxides or RE oxides were reported to have high pinning forces [3, 4]. The addition of RE oxides into REBCO was also reported to be effective in enhancing the $J_c$-$B$ performance of pulsed-laser-deposited YBCO films and sintered films [5-7]. Very recently, we have reported the enhanced $J_c$-$B$ performance of FF-MOD-REBCO films achieved by Ho addition [8]. However, there are few reports on the effects of RE$_2$O$_3$ or RE addition on MOD films.

In the present study, we have investigated the effects of lanthanum (La) addition on the superconducting properties and crystal growth of REBCO (RE = Gd, Sm and Dy) films fabricated by the FF-MOD method.

2. Experimental
The starting solutions for REBCO (RE = Gd, Sm and Dy) films were prepared by mixing stoichiometric amounts of Gd-, Sm-, Dy-, Ba-, and Cu-2-ethylhexanate (2-EH) solutions (Nihon Kagaku Sangyo Co., Ltd.). La-added REBCO films were fabricated by mixing REBCO solutions with 0.5, 1.0, 3.0, 5.0, and 10.0 mol% La-2-EH. The pure and La-added REBCO precursor films were fabricated by coating the mixed solutions on LaAlO$_3$ (100) single-crystal substrates, dried at 120°C for 30 min, and then calcined at 600°C for 30 min in air. The coating and calcination procedure was repeated three times. The precursor films were fired at a heating rate of 5°C/min from 840°C to 900°C, kept at 900°C for 30 min, and then cooled to room temperature in flowing N$_2$ gas with an oxygen content of less than 2 ppm. Finally, the films were annealed at 350°C for 2 h in O$_2$. The phases in the films were identified by X-ray diffractometry (XRD) with CuKα radiation. The electrical resistivity of the films was measured by the standard four-probe technique to determine the critical temperature ($T_c$) values. The $J_c$ values of the films under varying magnetic fields ($0 < B < 1$ T) were calculated from $B-M$ curves obtained by a superconducting quantum interference device, by using an extended version of Bean’s critical state model [5]. The surface of the films was characterized by scanning electron microscopy (SEM).

3. Results and Discussion

Figure 1 shows the La content dependence of the surface SEM images for the GdBCO, SmBCO and DyBCO films. Many holes were observed for the surface of the pure GdBCO film (figure 1(a)). The GdBCO film with La addition below 3 mol% showed decrease in the average number density of holes on the film surface from 17.3 to 2.8 in the area of $10 \times 10$ µm$^2$. The average size of the hole for the GdBCO film without and with 3 mol% La addition was estimated to be 0.36 µm and 0.18 µm, respectively. This indicated that the number density of holes and relatively large holes were decreased by 3 mol%-La addition. The GdBCO film with La addition over 3 mol% showed cracks on the surface. A large number of fine grains due to the poor grain growth were observed for the pure DyBCO surface (figure 1(g)). The La-added DyBCO film over 3 mol% showed the relatively flat and dense surface. These results suggest that La addition has effects on the improvement of the surface flatness and decrease in the hole density for the MOD-GdBCO, SmBCO and DyBCO films.

![Figure 1. SEM images of pure and La-added REBCO film surfaces.](image-url)
Figure 2 shows the dependence of the (006) XRD peak intensity on La content for GdBCO, SmBCO and DyBCO films. For the GdBCO film, as the amount of La addition increased, the XRD peak intensity increased up to 3 mol% and decreased thereafter. This indicates that a La addition of up to 3 mol% enhances the crystal growth of the superconducting phase. SmBCO and DyBCO films showed an increase in XRD peak intensity with La addition. In particular, the increase in the XRD peak intensity for the DyBCO films agrees with the results from the SEM analysis in figures 1(g) and 1(h). These results suggest that La addition is effective in promoting the crystallization and/or crystal growth of the superconducting phase. The decrease in the number density of holes on the film surface and the promotion of the film crystallization may relate to the improved lattice matching between REBCO and pseudo-cubic LAO with a lattice constant of \( a = 3.79 \, \text{Å} \), because of the decrease in the lattice constants of \( a \) and \( b \) by the La substitution for the Ba site in the REBCO structure as reported for La(Ba\(_{2-x}\)La\(_x\))CuO\(_y\) [9], or the decrease in the \( b \)-axis for Y(Ba\(_{2-x}\)La\(_x\))CuO\(_y\) compound [10].

![Graph of Intensity vs. La addition](image)

**Figure 2.** Dependence of (006) XRD peak intensity on La addition for REBCO films.

Figure 3 shows the \( J_c \)-\( B \) performance for the GdBCO, SmBCO, and DyBCO films. The \( T_c \) values for pure and La-added REBCO films were measured to be 89 - 90 K. The La-added GdBCO film showed an improved \( J_c \)-\( B \) performance compared to the pure GdBCO film below 3 mol% (figure 3(a)). This agrees with the trend revealed by the SEM (figure 1) and XRD analyses (figure 2). The \( J_c \) value at the self-magnetic field for the 1 mol%-La-added-GdBCO film (2.38 MA/cm\(^2\)) was 1.8 times as high as that of the pure GdBCO film (1.32 MA/cm\(^2\)). The \( J_c \)-\( B \) performance also improved upon La addition in the case of the SmBCO and DyBCO films. The \( J_c \) at the self-magnetic field for the 3-mol%-La-added SmBCO film increased by a factor of four compared to the pure SmBCO film. The 3-mol%-La-doped DyBCO film showed a \( J_c \) of 0.89 MA/cm\(^2\), even though the pure DyBCO film with \( T_c \) of 89 K showed no superconducting current. The enhancement in the self-magnetic field \( J_c \) and the \( J_c \)-\( B \) performance of the La-added films was presumably due to the decrease in the number density of holes on the film surface and improved crystallinity induced by La addition, as discussed in figures 1 and 2.

\( J_c \) is known to be proportional to \( B^\alpha \) under a relatively low magnetic field (0 ≤ \( B \) ≤ 1 T) [11-12]. Here, the power exponent \( \alpha \) is a parameter for describing the pinning performance in superconducting thin films under a magnetic field: a smaller \( \alpha \) value means higher \( J_c \)-\( B \) performance. The La content dependence of \( \alpha \) for La-added REBCO films is shown in figure 4. The \( \alpha \) value of the GdBCO and DyBCO films was almost constant below a La content of 3 mol%, and increased with increasing La content above 3 mol%. By contrast, the \( \alpha \) values of the SmBCO films showed a decreasing trend with increasing La content. The lowest \( \alpha \) for La-added REBCO films was approximately 0.72, which is
comparable to the $\alpha$ values of the Ho-added MOD-GdBCO films in our previous study [8]. A relatively low $\alpha$ value of 0.53 is reported for MOD-REBCO thin films with a pinning center such as BaZrO$_3$ [13]. Therefore, we speculate that the decrease in $\alpha$ is due to the improvement in the number density of holes on the film surface and crystallinity of the films.

Figure 3. Magnetic field dependence of $J_c$ for pure and La-added REBCO films at 77 K: (a) GdBCO, (b) SmBCO, and (c) DyBCO films.

Figure 5 shows the dependence of $c$-axis length on La addition for GdBCO, SmBCO, and DyBCO films. All the films expect the SmBCO exhibited the same trend: The $c$-axis length increased with increasing La content. This increase was presumably caused by the partial substitution of La for the

Figure 4. La addition dependence of $\alpha$ values for pure and La-added REBCO films.

Figure 5. Dependence of $c$-axis length on La addition for REBCO films.
Gd, Sm, and Dy sites in the REBCO structure, given the larger ionic radius of La$^{3+}$ (0.105 nm) as compared to those of Gd$^{3+}$ (0.094 nm), Sm$^{3+}$ (0.096 nm), and Dy$^{3+}$ (0.091 nm). Furthermore, the change in the c-axis length of the DyBCO film was greater than that of the SmBCO film, which is attributable to the difference in ionic radius between Dy$^{3+}$ and Sm$^{3+}$.

4. Conclusions
We have investigated the effects of La addition on the superconducting properties and crystal growth of REBCO films (RE = Gd, Sm, and Dy) fabricated by the FF-MOD method using 2-ethylhexanate solutions. La-doped REBCO films showed an improvement in surface flatness and a decrease in density of holes on the surface. The SEM and XRD results suggested that La addition was effective in promoting crystallization and crystal growth of the superconducting phase. In particular, for the 1 mol%-La-added-GdBCO film, the $J_c$ value at the self-magnetic field improved 1.8-fold (2.38 MA/cm$^2$) relative to the corresponding value for the pure GdBCO film (1.32 MA/cm$^2$). However, the $J_c$-$B$ performance did not improve upon La addition in the case of the REBCO films.

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