Improvement of in-field performance for EuBCO with heavily doped BHO coated conductors by PLD method with high temperature deposition and low temperature annealing

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Abstract. Recently, we have found that BaHfO3 (BHO)-doped EuBa2Cu3O7-X (EuBCO) coated conductors by the combination of the IBAD and PLD methods show high critical current (Ic) even in an applied magnetic field. However, for the wide application of BaMO3 (BMO, M: metal)-doped REBa2Cu3O7-X (REBCO) coated conductors to industrial and commercial applications, much higher in-field performance is required. It is known that the critical temperature (Tc) of BMO-doped REBCO layers, especially by the PLD method, decreases with the increase in the amount of doped BMO apparently due to the strain of the REBCO induced by BMO doping. Therefore, it is difficult to improve the critical current density (Jc) in the applied magnetic field of BMO doped REBCO coated conductors only by increasing the quantity of BMO especially at high temperatures such as 77 K. To solve this problem, we tried to optimize the deposition conditions, especially the deposition temperature and O2 annealing processes for heavily BHO doped-EuBCO layers fabricated by the PLD method. As a result, the combination of high temperature deposition and low temperature O2 annealing was effective in obtaining high Tc and high in-field performance of heavily BMO-doped REBCO coated conductors. The Tc of 10 mol% BHO-doped EuBCO coated conductors was 93.9 K (setting a deposition temperature of 1150 °C and O2 annealing temperature of 280 °C) which is nearly the same as that for non-doped EuBCO coated conductors. On the other hand, over-doping is preferred for high in-field Jc. Therefore, a high Jc under a magnetic field was obtained in the BHO-doped REBCO layer annealed at a low temperature. The Jc (min.) of 5 mol% BHO-doped EuBCO coated conductors was 0.62 MA/cm2 at 77 K and 3 T (setting deposition temperature of 1150 °C and O2 annealing temperature of 250 °C). Using these results, we confirm the successful fabrication of heavily BHO-doped EuBCO coated conductors showing high in-field performance by the PLD method.

1. Introduction

Long artificial pinning centers (APCs)-doped REBa2Cu3O7-X (REBCO, RE: rare earth element) coated conductors are being developed for industrial and commercial applications. Recently, APCs-doped and non-doped REBCO coated conductors having length ranging from several hundred meters to several kilometers are being commercialized by many companies around the world. We have been
also investigated BaMO$_3$ (BMO, M: metal) doped and non-doped long REBCO coated conductors by the combination of the ion-beam assisted deposition (IBAD) [1, 2] and pulsed laser deposition (PLD) methods [3-16]. In recent years, it has been found that BaHfO$_3$ (BHO)-doped EuBa$_2$Cu$_3$O$_{7-\delta}$ (EuBCO) coated conductors by the IBAD/PLD method is effective for obtaining high in-field performance. The BHO-doped EuBCO coated conductor shows a high critical current ($I_c$) of 144 A/cm-W at 77 K in 3 T and 411 A/cm-W at 65 K in 3 T [17]. Especially, we optimized the growth conditions of BHO-doped EuBCO layers by which the mode of EuBCO layer growth changed from the vapor-solid (VS) mode to the vapor-liquid-solid (VLS) mode in order to deposit BHO-doped EuBCO layers having high superconducting characteristics [18]. Furthermore, we can fabricate 100 - 200 m long BHO-doped EuBCO layers at high production rate and maintaining high in-field performance over the entire length [19]. However, the $I_c$ values in the magnetic field at high temperature of long BMO-doped REBCO coated conductors need to be further improved for industrial and commercial applications.

As a candidate, it is thought to be effective in increasing the doping amount of BMO for further improvement of the in-field performance of BMO-doped REBCO coated conductors. However, it is known that the critical temperature ($T_c$) of REBCO layers decreases with the increase in the amount of BMO for the vapor deposition process including the PLD method because of the strain of the REBCO phase by BMO doping [20, 21]. Therefore, it is difficult to improve the critical current density ($J_c$) in the applied magnetic field of BMO-doped REBCO coated conductors simply by increasing doping amount of BMO. To prevent the reduction of $T_c$ and $J_c$ of the REBCO layers as the quantity of BMO increases, we tried to optimize the deposition conditions, especially the deposition temperature and O$_2$ annealing processes for BHO-doped EuBCO layers fabricated by the PLD method. As a result, we improved the in-field performance of heavily BHO-doped EuBCO layers by the PLD method with high temperature deposition and low temperature O$_2$ annealing process.

2. Experimental details
BHO-doped EuBCO layer underwent deposition by a Reel-to-Reel PLD system on 10 mm wide CeO$_2$ (300 - 700 nm) / LaMnO$_3$ (7 nm) / IBAD-MgO (5 nm) / Y$_2$O$_3$ (14 nm) / Gd$_2$Zr$_2$O$_7$ (56 nm) / Hastelloy C276 (100 $\mu$m) substrates (Fig. 1). The value of in-plane and out-of-plane degrees of texturing ($\Delta\phi$ and $\Delta\omega$) of the CeO$_2$ cap layer were approximately 1 - 3 $^\circ$ and 0.5 - 1 $^\circ$ degrees, respectively. The texture of the CeO$_2$ and BHO-doped EuBCO layers were measured by the analysis of the X-ray diffraction pattern and X-ray pole figure. The $\Delta\omega$ (full width at half maximum of the X-ray diffraction rocking curve) and $\Delta\phi$ (full width at half maximum from X-ray F-scan of the CeO$_2$ (220) and BHO-doped EuBCO (103) peak) were applied as the out-of-plane and in-plane texturing degrees, respectively. A 200 W industrial XeCl excimer laser with a wavelength of 308 nm and typical pulse duration (FWHM) of approximately 22 ns was used at a pulse energy in the range of 500 - 600 mJ (the size of the laser beam is approximately 420 mm$^2$) and a pulse repetition rate of 177 Hz. The optical system is synchronized to the laser pulse and scanning of the laser beam on a sintered the BHO-doped EuBCO target was also controlled. The laser repetition rate at 177 Hz is divided into 4 plumes which are nearly identical in size and shape (Fig. 2). The laser energy density directly above the sintered the BHO-doped EuBCO target is approximately 2 - 3 J/cm$^2$. To realize the VLS growth mode for BHO-doped EuBCO layers, we used the commercially available sintered target of off-stoichiometric EuBa$_2$Cu$_3$O$_{7-\delta}$ containing 3.5 - 10 mol% doped BHO with a diameter of 6 inches and a thickness of 5 mm for BHO-doped EuBCO layer depositions. The amount of BHO doped is 3.5, 5, 7.5 and 10 mol% correspondings to approximately 1.5 vol%, 2.1 vol%, 3.3 vol% and 4.4 vol%, respectively. Typically, the pulse repetition rate of 177 Hz and pulse energy of 500 - 600 mJ cause a deposition rate of approximately12 nm/s for a BHO-doped EuBCO layer. The setting deposition temperatures were 1035 - 1150 $^\circ$C for a substrate with a transfer speed of 30 m/h. The setting deposition temperatures were determined from the surface temperature of the CeO$_2$ layer measured using a K-type thermocouple. The surface temperature of the CeO$_2$ layer was approximately 880 $^\circ$ C when the setting deposition temperature was 1095 $^\circ$ C. The oxygen pressure was maintained at 600 mTorr (80 Pa) with a flow of 10 sccm (standard cubic centimeter per minute) oxygen. The T-S (distance between the sintered BHO-
doped EuBCO target and the substrate) was set at 90 - 100 mm. The typical thickness value of a BHO-doped EuBCO layer was in the range of 0.50 – 0.55 \( \mu \text{m} \) for one time deposition with a substrate transfer speed of 30 m/h. The \( I_c \) value was measured by the conventional four-terminal method with a criterion of 1 \( \mu \text{V/cm} \). The \( J_c \) value of the BHO-doped EuBCO coated conductors was calculated from the cross-sectional area of a BHO-doped EuBCO layer. The thickness and cross-section images of the BHO-doped EuBCO layer were observed using a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Samples several centimeters in length were cut out from the ends of long BHO-doped EuBCO coated conductors to examine the angular dependence of \( I_c \) values on the applied magnetic field angle, which was changed from 0 to 180 ° to the \( c \)-axis (180 ° corresponds to a magnetic field parallel to the \( c \)-axis direction).

Figure 1. Schematic diagram of our BHO-doped EuBCO coated conductors by IBAD/PLD method.

Figure 2. Schematic diagram of our multi-plume and multi-turn (MPMT) PLD method.

3. Results and discussion
We fabricated 10 mol% BHO-doped EuBCO coated conductors at several different deposition temperatures by the PLD method. Figure 3 shows the TEM cross-section images of 10 mol% BHO-doped EuBCO coated conductors that underwent (a) low temperature (1095 °C) deposition and (b) high temperature (1135 °C) deposition. Although both have nearly the same structure, the BHO-doped EuBCO coated conductor obtained through low temperature deposition seems to have a slight decrease in the straightness of the distribution of BHO nano-rods compared to a BHO-doped EuBCO coated conductor at high temperature deposition. The difference in the distribution of BHO nano-rods is considered to be due to the deposition temperature [22]. The EuBCO and BHO phases grow at the same interface. The BHO nano-rod is formed due to the interfacial energy between the EuBCO and BHO. If the interfacial energy is large enough comparing with the supersaturation, which is the driving force of the overall growth, the BHO phase should be continually grown. On the other hand, if the interfacial energy is relatively small, the degree of continuity and straightness of the nano-rod should deteriorate. Because the growth at a low temperature means high supersaturation, which might lead to the latter ease, the short rods are tilted in the film grown at a low temperature.

Figure 4 shows the setting deposition temperature dependence of (a) \( T_c \) and \( I_c \) at 77 K in a self-field and (b) \( T_c \) and \( c \)-axis length of 10 mol% BHO-doped EuBCO coated conductors. The 10 mol% BHO-doped EuBCO coated conductors showed a high \( T_c \) of 93.9 K. The \( T_c \) and \( c \)-axis length of 10 mol% BHO-doped EuBCO coated conductors were improved by high temperature deposition. It is considered that EuBCO phase is stretched by the strain between EuBCO phase and BHO rods as a cause of low \( T_c \) and long \( c \)-axis length at low temperature deposition. Figure 5 shows the schematic diagram of the reason for the improvement of \( T_c \) and \( c \)-axis length. The strain in REBCO phase surrounding the BMO rods is suppressed by high temperature deposition, since the plasticities of both phases may the higher at high temperatures. The decrease in \( T_c \) is attributed to be distortion of the
REBCO phase in the vicinity of the BMO phase due to the difference in lattice constant between the REBCO and BMO phases. It is thought that strain regions are reduced by high temperature deposition.

We fabricated 3.5, 5, 7.5 and 10 mol% BHO-doped EuBCO coated conductors by the PLD method with a high deposition temperature of 1150 °C. Additionally, we tried to anneal it for oxygen doping at a low temperature of 250 °C. Figure 6 shows the schematic diagram of our O₂ annealing profile for BHO-doped EuBCO coated conductors by the PLD method. Figure 7 shows the effect of doping on BHO dependence of $J_c$ at 77 K in the self-field of BHO-doped EuBCO coated conductors. Critical currents were measured by the conventional four-terminal method in laser patterned surface of BHO-doped EuBCO layers with bridges 10 - 20 μm in width. $J_c$ values of EuBCO with a doping of up to 5 mol% BHO coated conductors were improved compared to the same value as non-doped EuBCO coated conductor by low temperature O₂ annealing. It is expected that the EuBCO phase is in an over-doped state because the $J_c$ value increases although $T_c$ is decreases by low temperature O₂ annealing.

From these results, high temperature deposition and low temperature O₂ annealing are effective in improving the $T_c$ and $J_c$ at 77 K in the self-field for BMO-doped REBCO coated conductors by the PLD method.

![Figure 3](image1.png)

**Figure 3.** TEM cross-section images of 10 mol% BHO doped EuBCO coated conductors with (a) low temperature (1095 °C) deposition and (b) high temperature (1135 °C) deposition. Although both have nearly the same structure, BHO doped EuBCO coated conductor with low temperature deposition seems to have a slight decrease in straightness of the BHO nano-rod distribution compared to BHO-doped EuBCO coated conductor with high temperature deposition.

![Figure 4](image2.png)

**Figure 4.** Setting deposition temperature dependence of (a) $T_c$ and $J_c$ at 77 K in the self-field and (b) $T_c$ and c-axis length of 10 mol% BHO-doped EuBCO coated conductors. The 10 mol% BHO-doped EuBCO coated conductors showed a high $T_c$ of 93.9 K by high temperature deposition (setting deposition temperature of 1150 °C and O₂ annealing temperature of 280 °C), which is almost same as a non-doped EuBCO coated conductors.
Figure 5. Schematic diagram of improved suppression of strain regions between BMO (APCs) doped REBCO phase by high temperature deposition. The cause of $T_c$ decrease is considered to be the distortion of the REBCO phase in the vicinity of the BMO phase due to the difference in lattice constant between these phases. It is thought that strain regions are reduced by high temperature deposition.

Figure 6. Schematic diagram of our O$_2$ annealing profile for BHO doped EuBCO coated conductors by PLD method.

Figure 7. Plot of $J_c$ vs. quantity of BHO at 77 K in self-field of BHO doped EuBCO coated conductors by PLD method. $J_c$ values of EuBCO with a doping of up to 5 mol% BHO coated conductors were improved to the same value as non-doped EuBCO coated conductor by low temperature O$_2$ annealing.

On the other hand, we examined the effect on the improvement of high superconducting characteristics of BMO-doped REBCO coated conductors by the PLD method with low temperature
O₂ annealing only. Figure 8 shows the setting deposition temperature dependence of $I_c$ at 77 K in the self-field of 5 mol% BHO-doped EuBCO coated conductors by the PLD method with the low temperature of O₂ annealing. It can be considered that the $T_c$ value is improved by reducing the strain at the interface between the EuBCO and BHO phases due to high temperature deposition. Furthermore, the over-doped state is realized because the O₂ is easily diffused into the BHO-doped EuBCO phase during the annealing process thereby reducing the strain. Therefore, heavily BHO-doped EuBCO coated conductors does not obtain high superconducting characteristics by high temperature deposition and low temperature O₂ annealing alone.

Figure 8. Plot of $I_c$ vs. setting deposition temperature at 77 K in the self-field of 5 mol% BHO-doped EuBCO coated conductors by PLD method with low temperature annealing. Good in-field performance heavily BHO-doped EuBCO coated conductors is not obtained by high temperature deposition and low temperature annealing alone.

We fabricated 3.5, 5, 7.5 and 10 mol% BHO-doped EuBCO coated conductors by the PLD method with a high setting deposition temperature of 1150 °C and low O₂ annealing temperature of 250 °C. Figure 9 indicates (a) the magnetic field dependence of $J_c$ for 3.5, 5, 7.5 and 10 mol% BHO-doped EuBCO coated conductors and (b) the magnetic field angular dependence of $J_c$ at 77 K in 3 T for 3.5, 5, 7.5 and 10 mol% BHO-doped EuBCO coated conductors by the PLD method with laser patterned surface of BHO-doped EuBCO layers with bridges 10 - 20 μm in width. The $J_c$ (min.) of 5 mol% BHO-doped EuBCO coated conductor was approximately 0.62 MA/cm² at 77 K in 3 T. Clear improvement in the in-field performance for 5 mol% BHO-doped EuBCO coated conductors can be recognized in $J_c$-B-θ properties too by high temperature deposition and low temperature O₂ annealing. It seems that the $J_c$-B-θ properties depending on the quantity of BHO and manner of distribution of BHO nano-rods in the EuBCO layer. However, the correlation and trend between the amount of BHO doping and $J_c$-B-θ properties have not yet been clarified. It should be discussed based on further microstructural analysis.

Although the $T_c$ of 10 mol% BHO-doped EuBCO coated conductor was improved (from Fig. 4) by using high temperature deposition and low temperature O₂ annealing, and it is considered that the improvement of superconducting characteristics is locally achieved because the $J_c$ at 77 K and the self-field decreases as the proportion of doped BHO increases (from Fig. 7). The in-field performance were improved since the pinning effect is stronger in the relatively rightly BHO-doped (3.5 -5 mol%) EuBCO coated conductors, but it is thought that the in-field performance also deteriorated in the EuBCO with heavily BHO-doped (7.5 - 10 mol%) EuBCO coated conductors. Therefore, to improve the $J_c$ at self and magnetic field of more heavily BMO-doped REBCO coated conductors, it is necessary to improve both high temperature deposition and low temperature O₂ annealing process.
Figure 9. (a) magnetic field dependence of $J_c$ for 3.5, 5, 7.5 and 10 mol% BHO-doped EuBCO coated conductors and (b) magnetic field angular dependence of $J_c$ at 77 K in 3 T of 3.5, 5, 7.5 and 10 mol% BHO-doped EuBCO coated conductors by PLD method. The $J_c$ (min.) of 5 mol% BHO-doped EuBCO coated conductor was about 0.62 MA/cm$^2$ at 77 K in 3 T.

4. Conclusions

We tried to optimize the fabricating conditions in the PLD method, especially the deposition temperature and O$_2$ annealing processes to reduce the reduction of $T_c$ and $J_c$ of REBCO layers with simply increasing the amount of BMO because of the strain of the REBCO by doping of BMO. We fabricated 3.5, 5, 7.5 and 10 mol% BHO-doped EuBCO coated conductors by the PLD method with high setting deposition temperature of 1150 °C and low O$_2$ annealing temperature of 250 °C. Conventionally, 3.5 mol% BHO-doped EuBCO coated conductors showed the highest in-field performance in our laboratory. However, by using the high temperature deposition and low temperature annealing processes, the $T_c$ of 10 mol% BHO-doped EuBCO was improved to almost the same value of 93.9 K as pure-EuBCO (non BHO-doped EuBCO) coated conductors and the 5 mol% BHO-doped EuBCO coated conductor had the highest $J_c$ (min.) at 77 K in 3 T of approximately 0.62 MA/cm$^2$. The cause of $T_c$ decrease is considered to be the distortion of the REBCO phase in the vicinity of BMO phase due to the difference in lattice constant between the REBCO and BMO phases, resulting in a situation in which oxygen finds it difficult to enter the REBCO phase. It is thought that these strain regions are reduced by high temperature deposition and REBCO is in an over-doped state.
by low temperature O$_2$ annealing. From these results, we improved the in-field performance of heavily BMO-doped REBCO using the PLD method with high temperature deposition and low temperature O$_2$ annealing.

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5. References
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