Superconducting properties and microstructure of PLD-
ErBa$_2$Cu$_3$O$_{7-\delta}$ films with BaNb$_2$O$_6$

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Abstract. We report superconducting properties and microstructures of ErBa$_2$Cu$_3$O$_{7-\delta}$ (ErBCO) films with BaNb$_2$O$_6$ (BNO) grown by Pulsed Laser Deposition (PLD) on SrTiO$_3$ (STO) substrates. The BNO was introduced into the ErBCO films as an artificial pinning center. X-ray diffraction analysis indicated the high orientation both c-axis and in-plane for the obtained ErBCO films. An ErBCO film with BNO-doping (BNO + ErBCO) maintained the high critical temperature ($T_c$) comparison with an ErBCO film with BZO-doping (BZO + ErBCO). Nanorods were observed clearly in Transmission Electron Microscopy (TEM) images of the BNO+ErBCO films. The nanorod diameter was smaller with lower substrate temperature during deposition. The BNO + ErBCO films showed higher critical current density ($J_c$) than that of a pure ErBCO film for field//c-axis. Furthermore, we confirmed a tendency that $J_c$ of the BNO+ErBCO films were enhanced with lower substrate temperature. This indicates that nanorods observed in cross-sectional TEM images affected as c-axis correlated pinning centers.
We suggest that the BNO is effective as a pinning material for ErBCO film with maintaining high $T_c$.

1. Introduction
Recently, improvement of superconducting properties has been proceeded by introducing pinning centers into REBa$_2$Cu$_3$O$_{7-\delta}$ (REBCO, RE: rare earth elements) superconducting materials. We have been focusing on ErBCO since this material has higher $T_c$ comparing with that of YBCO[1]. And, has no substitution problems between RE and Ba atoms in ErBCO. Furthermore, oxygen contents in the ErBCO can be easily controlled comparing with other REBCO. Improvement of $J_c$ performance for an ErBCO film was demonstrated by introduction of pinning centers into the ErBCO in various external magnetic fields at 77K. BaZrO$_3$ (BZO)-doped ErBCO films grown on STO substrates were reported to have $c$-axis correlated pinning centers[2,3,4]. In these papers, it is recognized that the dispersed BZO regions (which is called as a nanorod[2]) in the ErBCO film was effective as pinning centers. However, with increasing the amount of BZO-doping into the ErBCO films, $T_c$s of the films are degraded drastically. Introduction of pinning centers in an ErBCO film with maintaining $T_c$ is important for realizing the high $J_c$ in external magnetic fields.

It was found that high $T_c$ properties were maintained in the bulk ErBCO with BNO which has a different crystal structure from a cubic perovskite of BZO[5]. $T_{c_{on}}$ and $T_{c_{zero}}$ for bulk ErBCO with 1.5 wt% BNO, were reported to be 95K and 93K respectively [6].

In this study, we grow ErBCO films with BNO doping on STO substrates and investigate superconducting properties and microstructures of the BNO + ErBCO films. We investigated about effects of crystallization factors such as growth temperature, and discussed relationship between the $J_c$ properties in magnetic fields.

2. Experimental
2.1. Growth of ErBCO films
We grew BNO+ErBCO films on (100)-oriented STO substrates (10mm×10mm) by a PLD technique. A Lambda Physik Ar-F excimer laser (wave length = 193 nm) was used for laser ablation. A sintered ErBCO ceramic bulk was used as a target for the deposition, which contains BNO in the concentration range between 0 wt% and 5 wt% BNO. The target diameter and thickness are 40mm and 5mm, respectively. The target was ablated by the high-energy laser, then the film consisted of the objective composition was grown on the confronted substrate to the target. During the film growth, both the target and the substrate were rotated to obtain the uniform composition and thickness of the film. The substrate was fixed with silver paste to a metal-substrate holder, which was heated by a lamp heater.

The substrate temperatures for the BNO+ErBCO film growth were varied between 710 °C and 760 °C. The substrate temperature was monitored by a thermocouple and calibrated by an optical pyrometer. The laser frequency was 1Hz and the laser energy was 400 mJ. The deposition time of BNO+ErBCO films was 60 min. During deposition, the O$_2$ background pressure was fixed at 400 mTorr. Ex-situ post-annealing was performed at 450°C for 15 min in flowing oxygen after the film growth. After the O$_2$ annealing, the film was cooled rapidly to room temperature to preserve the oxygen contents of the BNO+ErBCO films at the annealed temperatures.

2.2. Evaluation of grown films
Preferred orientation of the grown BNO+ErBCO films in this study was evaluated by X-ray θ/2θ diffraction with Cu-Kα radiation. In-plane orientation of the BNO+ErBCO films was evaluated by X-ray φ-scan by using an (102) plane of ErBCO. The magnetic fields dependence of $J_c$ ($I_c$-B) was measured by a conventional four-probe method in magnetic fields of 0 to 3T. The lattice images and grain azimuth of the films were observed by TEM.
3.1. Crystallinity of BNO+ErBCO films

Figure 1 shows a typical X-ray $\theta/2\theta$ diffraction pattern of BNO+ErBCO films. $00l$ peaks of ErBCO were detected, which indicated the film was $c$-axis oriented. Furthermore, an additional peak was observed around $44^\circ$ in diffraction pattern for the BNO+ErBCO films. This peak was confirmed only in the ErBCO film with BNO-doping, which increases with increasing the BNO-doping concentration.

Figure 2 shows a typical X-ray $\phi$-scan diffraction pattern of the film. Each four peak was clearly detected in an interval of $90^\circ$, indicating that the film has a four-fold symmetry on the STO substrate. These diffraction patterns were essentially identical to those for all grown BNO+ErBCO films.

3.2. $T_c$ of BNO+ErBCO films

We evaluated $T_c$ of the BNO+ErBCO films in order to investigate the influence of the BNO-doping into ErBCO on superconducting properties. Figure 3 shows the variation of the $T_c$ as a function of the nominal concentration of BNO and BZO in the target for the ErBCO films grown at 730 °C. Here, $T_c$ of the BZO+ErBCO films were plotted to compare with that of BNO+ErBCO films. For BNO+ErBCO films, 1.5 wt% BNO+ErBCO film showed the highest $T_c$ of 87.7K. As can be seen in Fig 3, the $T_c$ decreased with increasing doping amount, with gradients of $-0.54K$ per wt% for BNO+ErBCO film and $-0.90K$ per wt% for BZO+ErBCO film. Although the lattice mismatch between ErBCO and BNO was higher than that for BZO, BNO+ErBCO films showed higher $T_c$ to high concentration of BNO. Furthermore, we investigated $T_c$ of the 1.5 wt% BNO+ErBCO films grown with varying growth temperatures. The $T_c$s were confirmed in range from 88 to 90K. The BNO+ErBCO films had maintained high $T_c$ of ErBCO under the growth condition because $T_c$s of the pure ErBCO films were around 89K.

Figure 1. A typical X-ray $\theta/2\theta$ diffraction pattern of BNO+ErBCO films.  
Figure 2. A typical X-ray $\phi$-scan diffraction pattern of BNO+ErBCO films.  
Figure 3. The variation of the $T_c$ as a function of the nominal concentration of BNO and BZO in the target for the annealed ErBCO films grown at 730 °C.
3.3. Cross-sectional observation of BNO +ErBCO films
Cross-sectional images of the 1.5 wt% BNO+ErBCO films were observed in order to investigate microstructures in the films by TEM. Figures 4 and 5 show cross-sectional TEM images of 1.5 wt% BNO+ErBCO films grown at 730 °C and 760 °C, respectively. Nanorods were clearly observed in the both films. The typical nanorods are shown by arrows in Figs.4 and 5. It was recognized that the BNO-doping induced defects into ErBCO film. It was thought that an additional peak detected by X-ray θ/2θ diffraction pattern originated in these nanorods. Then it was thought that the expanded nanorod structures were formed and aligned along c-axis direction of ErBCO. The boundaries between nanorods and the epitaxially grown ErBCO grains were suggested to be effective pinning centers. Nanorods were distributed into entire film and the diameter of nanorods in Figs.4 and 5 are from 4 nm to 7 nm and from 6 nm to 22 nm, respectively. The average diameter of a nanorod increases with substrate temperature in the constant BNO-doping amount. It was thought that this difference of the nanorod diameters depended on the nucleus migration length. That is, the defect size was controlled by the optimization of growth condition such as growth temperature. We considered that this result will be possible to introduce an effective pinning center into a superconducting film.

![Figure 4](image-url)  
**Figure 4.** Cross-sectional TEM image of 1.5 wt% BNO+ErBCO films grown at 730°C.

![Figure 5](image-url)  
**Figure 5.** Cross-sectional TEM image of 1.5 wt% BNO+ErBCO films grown at 760°C.

3.4. Critical current properties of BNO+ErBCO films
We observed $J_C$-B curves of the 1.5 wt% BNO+ErBCO films to investigate the pinning effect with BNO-doping under various substrate temperatures. Figure 6 shows magnetic fields dependences of the normalized $J_C [J_C / J_C (H=0)]$ for the films under external magnetic fields from 0 to 3 T at 77K. For the BNO+ErBCO films, normalized $J_C$ for H//c-axis were enhanced comparing with that of the pure ErBCO under the external magnetic field. This indicates that nanorods observed in cross-sectional TEM images affected as c-axis correlated pinning centers. In case of comparison with substrate temperature, the BNO+ErBCO film grown at 710°C showed the highest $J_C$ on all measured magnetic fields. Furthermore, we can see a tendency that $J_C$ of the BNO+ErBCO films were enhanced with lower substrate temperature. We suggested that a nanorod diameter was smaller with lower substrate temperature side by TEM images. From the nucleus migration length dependence of the nanorod diameter, nanorods were effective as pinning centers in smaller diameter with lower temperature growth.
4. Conclusion
We grew the BNO+ErBCO films on the STO substrate by PLD and investigated the superconducting properties and the microstructures of the films. The films were confirmed to be c-axis oriented and to have a four-fold symmetry on the STO substrate by X-ray diffraction patterns. $T_c$ of BNO+ErBCO films was higher than that of BZO+ErBCO films for high doping concentration. Furthermore, we focused especially about effects of crystallization factors such as growth temperature. The nanorods into ErBCO with BNO-doping were observed clearly in the TEM images. The average diameter of a nanorod increases with substrate temperature in the constant BNO doping amount. It was thought that this difference of the nanorod diameters depended on the nucleus migration length. And, the BNO+ErBCO films showed the $J_c$ enhancement for $H//c$-axis with lower substrate temperature. From observed TEM images, nanorods were effective as pinning centers in smaller diameter with lower temperature growth. It was confirmed that the BNO is effective as a pinning material with maintaining high $T_c$ of ErBCO.

References
[1] S. Horii, M. Mukaida, K. Matsumoto, T. Ohazama, A. Ichinose, Y. Yoshida, J. Shimoyama, K. Kishio, Physica C412-414 (2004) 1306.
[2] M. Mukaida, T. Horide, R. Kita, S. Horii, A. Ichinose, Y. Yoshida, O. Miura, K. Matsumoto, K. Yamada, N. Mori, Jpn. J. Appl. Phys. 44 (2005) L952.
[3] M. Ito, M. Mukaida, T. Ohazama, R. Kita, A. Ichinose, S. Horii, A. Saito, K. Matsumoto, Y. Yoshida, K. Koike, F. Hirose, A. Saito, S. Ohshima, Physica C 426-431 (2005) 1415.
[4] J. L. Macmanus-Driscoll, S. R. Foltyn, Q. X. Jia, H. Wang, A. Serquis, B. Maiorov, L. Civale, M. E. Hawley, M. P. Maley, and D. E. Peterson, Nat. Mater. 3, 439 (2004).
[5] F.H Francombe, Acta Cryst.13, (1960) 131
[6] R. Kita, private communication.