Crystallinity and in-field characterization of high-$T_c$ YBa$_2$Cu$_4$O$_8$ and Y$_{0.9}$Ca$_{0.1}$Ba$_2$Cu$_4$O$_8$ epitaxial films fabricated by low temperature flux method

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Abstract. REBa$_2$Cu$_4$O$_8$ superconductor has an important advantage that the critical temperature ($T_c$) is improved by Ca substitution for RE site. We fabricated the YBa$_2$Cu$_4$O$_8$ (Y124) and Y$_{0.9}$Ca$_{0.1}$Ba$_2$Cu$_4$O$_8$ (YCa124) films by molten hydroxide method in ambient atmosphere and investigated the crystallinity and in-field characterization. Obtained samples show that the film alignment is biaxial orientation and the grain size is larger than 50 $\mu$m, and the irreversibility field of YCa124 film is superior to that of Y124 in all the measured magnetic fields.

1. Introduction
For applications of the RE-Ba-Cu-O coated conductor operated at boiling temperature of liquid nitrogen (77.3 K) to various fields such as superconducting cable, transformer, the magnet and superconducting magnetic energy storage (SMES), an improvement of the coated conductors in critical current density ($J_c$) in magnetic fields is required. In the case of REBa$_2$Cu$_3$O$_y$ (RE123; RE: rare earth elements) coated conductors, a biaxial alignment of growth crystals, an introduction of pinning centers and the improvement of a critical temperature ($T_c$) have been greatly conducted. Although many groups have reported the improvement of $T_c$ in RE123 film by using liquid phase such as Ba-Cu-O flux [1, 2], these special techniques need a high growth temperature during film fabrication and cause degradation of superconducting properties due to impurity diffusion from metallic tape substrate.

The REBa$_2$Cu$_4$O$_8$ (RE124) has a rigorous stability of oxygen stoichiometry and no structural phase transition as opposed to RE123 phase. Moreover, RE124 keeps stable at far lower temperature than RE123 in the ambient atmosphere [3]. Although the $T_c$ of RE124 is inferior to RE123, the Y124 has an important advantage that the $T_c$ was improved by Ca substitution for RE site [4]. Single phase and single crystal of bulk RE124 phase are fabricated under high oxygen pressures about 400 atm and temperatures over 1000ºC [5]. 1-atm-pressure preparation is possible not only with addition of reaction enhancement reagents [6-8], but also by simple solid state reaction with extremely long annealing time. On the other hand, the preparation methods of single crystalline RE124 compound are reported by using molten alkali hydroxide in ambient atmosphere. Sandford et al. described synthesis of Eu124 single crystal from molten potassium hydroxide [9], Song et al. reported a more feasible
process for Y124 growth [10]. Recently, we achieved the synthesis of c-axis oriented RE124 epitaxial films fabricated by molten hydroxide method with low heating temperature of ~650°C, and we reported that the \( T_c \) of Ca-doped Y124 (YCa124) film achieved 90 K, which is 10 K higher than that of Y124 film [11].

In this investigation, we fabricated the biaxial oriented YCa124 films on NdGaO\(_3\) (NGO) substrate by molten hydroxide method and also discussed the crystallinity and in-field characterizations.

2. Experimental

Yttrium oxide, calcium carbonate, barium carbonate and copper oxide powders were used as starting materials, and potassium hydroxide (KOH) was used as a solvent. These starting materials were weighed with a total weight of 10 g with a molar ratio of Y : Ba : Cu = 1 : 2 : 4 and Y : Ca : Ba : O = 0.9 : 0.1 : 2 : 4 (amount of Y / Ca substitution \( x \) : 0.1) for Y124 and YCa124, respectively, and then mixed and put into alumina crucible with KOH of 100wt% to the raw materials. The NGO (001) single crystalline substrate was also put into the mixture. Then the mixture was heat-treated using a muffle furnace at 641°C for 12 hours in air. The obtained samples were washed in distilled water and ethanol using ultrasonic cleaning to eliminate the KOH and K\(_2\)CO\(_3\).

Phase identification and orientation were measured by X-ray diffraction (XRD) pattern with a CuK\( \alpha \) source. Grain size and surface morphology were obtained by scanning electron microscope (SEM). In-field characterization was measured by a standard four-probe method.

3. Results and discussion

3.1. Crystallinity

It is well known that the RE-Ba-Cu-O superconducting material has anisotropic physical properties due to layered crystal structure with alternating two-dimensional CuO\(_2\) planes, and the \( J_c \) along the CuO\(_2\) planes (\( // ab\)-plane) is superior to that of along the c-axis direction. Furthermore, in the case of RE123, the increase of misorientation angle between two grains causes serious degradation of \( J_c \), even for the c-axis oriented film [12].

The c-axis orientation of Y124 and YCa124 films are shown in Fig. 1, moreover, Fig. 2 shows in-plane orientation of (a) Y124 and (b) YCa124 films. It is revealed that the Y124 and YCa124 films showed sharp and intense diffraction patterns of the RE124 phase, and Y124 crystals grew epitaxially on NGO (001) substrate with 45° rotations in \( ab\)-plane direction. From these results, we can conclude that the Y124 and YCa124 film has biaxial alignment.

![Fig. 1 XRD 2\( \theta \)-\( \theta \) patterns of Y124 and YCa124 film](image1)

![Fig. 2 XRD 2\( \theta \)-\( \phi \) patterns (\( \phi \)-scan) of (a) Y124 and (b) YCa124 film. Diffraction peaks of both film and NGO substrate were observed by the Y124 (108) and NGO (204) reflection, respectively.](image2)
In order to discuss the crystallinity, we observed surface morphologies of Y124 and YCa124 films by SEM. Fig. 3 (a) and (b) shows SEM image of Y124 and YCa124 films, respectively. Both films have large grain size (> 50 μm). Moreover, it is found that the grain size was widened by Ca doping, and average grain size of YCa124 film achieve 100 μm. These results indicate that molten hydroxide method is novel technique for obtaining single crystalline film.

3.2. In-field characterization
For application of the RE-Ba-Cu-O, the improvement of the irreversibility field ($B_{irr}$) is important, and $B_{irr}$ was determined for understanding flux pinning states.

$R$-$T$ curves under $B // c$ and $B // ab$-plane for the Y124 film are shown in Fig. 4 (a) and (b), respectively. Broadening of the superconducting transition occurred by an applied magnetic fields. However, the degree of transition broadening largely depended on the $B$ direction, and the degree of transition broadening for the Y123 film under $B // c$ is obviously larger than that under $B // ab$, which is a typical behavior in Y123 films [13]. In this report, the transition broadening in $B // c$ for the Y124 film is larger than that in $B // ab$, as in the case of Y123 films. This indicates that the Y124 film has an intense pinning force due to intrinsic pinning by alternating stacked structure with blocking layer.

Fig. 5 shows the irreversibility line of Y124 and YCa124 films determined from $R$-$T$ curves under various magnetic fields. Interestingly, $B_{irr}$ of YCa124 film is superior to that of Y124 in all the measured magnetic fields. In order to discuss the difference of $B_{irr}$, we observed high-resolution SEM image of Y124 and YCa124 films. It was found that plenty of etch pits are present only in the YCa124 film (as shown in Fig. 6), and we can speculate that the $B_{irr}$ of YCa124 was enhanced by plenty of dislocation.

![Fig. 3 Surface morphology of (a) Y124 and (b) YCa124 films](image)

![Fig. 4 $R$-$T$ curves for Y124 film of (a) $B // c$ and (b) $B // ab$ in various magnetic field intensity](image)
4. Conclusion
We fabricated the Y124 and YCa124 films by molten hydroxide method in ambient atmosphere and investigated the crystallinity and in-field characterization. Y124 and YCa124 films show a biaxial orientation on NdGaO$_3$ (001) substrate with 45° rotations in $ab$-plane direction, and both films have large grain size (> 50 $\mu$m). Moreover, the grain size of film surface is wider up to 100 $\mu$m in the Ca substituted film. Broadening of the superconducting transition in $R$-$T$ curves is occurred by an applied magnetic fields, and transition broadening under $B$//$_c$ is larger than that under $B$//$_ab$. This indicates that the Y124 film has an intense intrinsic pinning such as RE123. Accordingly, the molten hydroxide method is suitable for the production of RE124 film with high crystalline perfection and in-field properties, which is an indispensable feature for reliable RE-Ba-Cu-O applications.

Acknowledgment
The authors appreciate of The Center for Integrated Research in Science, Shimane Univ. for in-field measurements.

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