Fabrication of Ca-doped REBa2Cu4O8 films by the molten hydroxide method

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Abstract

In order to improve a critical current density ($J_c$) under applied magnetic fields, it is well known that the RE-Ba-Cu-O superconductors are required an improvement of a critical temperature ($T_c$). Although the $T_c$ of REBa2Cu4O8 (RE124) is inferior to REBa2Cu3Oy (RE123), RE124 has rigorous stability of oxygen stoichiometry. Furthermore, the RE124 has an important advantage that the $T_c$ was improved by Ca-doping. In this study, in order to improve $T_c$ of RE124, we fabricated the Ca-doped RE124 (RECa124) films by using molten hydroxide method. The orientation of Y124 and YCa124 films showed a c-axis orientation completely and the $T_c$ of YCa124 film showed 10 K higher than that of the Y124 film. However, GdCa124 and SmCa124 films contained RE123 phase by much compare with YCa124 films and the $T_c$ were decreased with increasing of RE ionic radius over YCa124.

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Keywords: Superconducting film; Critical temperature; Molten hydroxide method

1. Introduction

In order to apply coated conductors to various fields such as superconducting cable, transformer, magnet and superconducting magnetic energy storage (SMES), a much more improvement of the coated conductors in critical current density ($J_c$) in magnetic fields is required. In the case of REBa2Cu3Oy (RE123; RE: rare earth elements) coated conductors, an introduction of artificial pinning centers (APC) and the improvement of a critical temperature ($T_c$) have been greatly conducted. Many groups have reported the improvement $T_c$ by using liquid phase such as Ba-Cu-O flux. Yun et al. demonstrated that the Nd123 films fabricated by tri-phase epitaxy using Ba-Cu-O flux showed a high $T_c$ = 94 K [1]. Recently, Ichino et al. reported that $T_c$ of La123 film was improved from 48.9 K to 71.5 K by vapor-liquid-solid growth mode [2]. However, these especial techniques need a high growth temperature during film fabrication and cause degradation of superconducting properties due to impurity diffusion from metallic tape substrate.

The REBa2Cu4O8 (RE124) was discovered as a stacking fault in RE123 film [3-5]. RE124 has a rigorous stability of oxygen stoichiometry and no structural phase transition. Moreover, RE124 resists H2O exposure and keeps stable in the ambient atmosphere. 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 [6]. Many preparation methods of RE124 film have been reported: sputtering [4], chemical vapor deposition [7, 8], electron-beam evaporation [9, 10], pulsed laser deposition [11, 12],
metal-organic decomposition [13], and others. However, some amount of RE123 phase is often formed in RE124 film. Single phase and single crystal of bulk RE124 phase are fabricated under high oxygen pressures about 400 atm and temperatures over 1000°C [14]. 1-atm-pressure preparation is possible not only with addition of reaction enhancement reagents [15-17], but also of 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 [18], Song et al. reported a more feasible process for Y124 growth [19] and Nagira et al. extended this method to the synthesis of RE124 with various rare earth elements [20].

In this investigation, we aim to fabricate crystalline films of RE124 and Ca-doped RE124 with high $T_c$ on a single crystalline substrate using molten hydroxide method and to clarify the effect of Ca-doping in crystallization and superconducting properties.

2. Experimental

Rare earth (RE = Yb, Er, Ho, Y, Gd, Sm) 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 RE : Ba : Cu = 1 : 2 : 4 and RE : Ca : Ba : O = 0.9 : 0.1 : 2 : 4 (amount of RE / Ca substitution: 0.1) for RE124 and RECa124, respectively, and then mixed and put into alumina crucible with KOH of 100wt% to the raw materials. The NdGaO$_3$ (001) single crystalline substrate was also put into the mixture. Then the mixture was heat-treated using a muffle furnace at 650°C for 12 hours in air. The obtained samples were washed by distilled water and ethanol using ultrasonic cleaning to eliminate the KOH and K$_2$CO$_3$.

The phase identification and lattice constant were measured by X-ray diffraction (XRD). Existence of superconducting phases and $T_c$ were determined by temperature dependence of magnetic susceptibility using superconducting quantum interference device (SQUID).

3. Results and discussion

We succeed the fabrication of crystalline films of almost stoichiometric RE124 and RECa124 with a thickness of ~15 μm on NdGaO$_3$ (001) single crystalline substrate. Fig. 1 shows XRD $2\theta$-$\theta$ patterns of films grown with raw material composition of (a) RE124 (RE124-film) and (b) RECa124 (RECa124-film). It is revealed that the RE124-films with smaller ionic radius elements of Yb, Er, Ho, Y showed sharp and intense diffractions patterns of the RE124 phase. However, the films with Er, Ho, Y showed a weak peak of RE123 (or RE123-related) and Ba-Cu-O related phases also. Furthermore, the peaks originated RE123 and Ba-Cu-O phases of the Gd124 and Sm124 film (with large ionic elements) are more than that of the films with smaller ionic radius elements. From these results, we can consider that the volume fraction of RE123 and Ba-Cu-O phases in matrix increased with increasing RE ionic radius.

![Fig. 1. XRD $2\theta$-$\theta$ patterns of (a) RE124-films and (b) RECa124-films.](image-url)
It is well known that the XRD 2θ-θ pattern contains the information of crystal lattice constant. The c-axis length was evaluated from 0026 diffraction (2θ ~94°), although the highest peak was identified to 0014 diffraction. It is because the peak of 0014 diffraction possibly includes 006 diffraction of RE123 phase and because the peaks with higher angles can generally evaluate more precise lattice constant than with lower angles. Fig. 2 shows c-axis length as a function of the RE ionic radius. The c-axis lengths of RE124- and RECa124-films were increased monotonically with increasing RE ionic radius and the c-axis length of RECa124-films were longer than that of RE124-films on several RE ions.

The \( T_c \) as a function of RE ionic radius is shown Fig. 3. The \( T_c \) of RE124-films (~80 K) is same as powder reports \([15, 16, 21]\). Moreover, the \( T_c \) of YCa124 film achieves 90 K, which is comparable to well-known Y123 phase. To clarify the effect of Ca-doping in superconducting properties on several RE ion, we calculated an enhancement value of \( T_c \) by subtracting \( T_c \) of RE124 from that of RECa124 (\( T_c^{RECa124} - T_c^{RE124} \)). Fig. 4 shows the \( T_c^{RECa124} - T_c^{RE124} \) as a function of RE ionic radius. The \( T_c^{RECa124} - T_c^{RE124} \) decreased by increasing with RE ionic radius larger than Y.

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**Fig. 2.** c-axis length of RE124- and RECa124-films as a function of RE ionic radius.

**Fig. 3.** \( T_c \) in RE124- and RECa124-films as a function of RE ionic radius.

**Fig. 4.** \( T_c^{RECa124} - T_c^{RE124} \) as a function of RE ionic radius.
Finally, we discuss the effect of Ca-doping in crystallization and superconducting properties. The ionic radius of Yb$^{3+}$, Er$^{3+}$, Ho$^{3+}$, Y$^{3+}$, Gd$^{3+}$, Sm$^{3+}$ are 0.985, 1.004, 1.015, 1.019, 1.053, 1.079Å, respectively [22]. Moreover, the ionic radius of Ca$^{2+}$ dopant is 1.12Å, and Ba$^{2+}$ is 1.35Å [22]. Considering from these ionic radius data, the $c$-axis length variation shown in Fig. 2 is reasonable when Ca$^{2+}$ is substituted for RE site in the crystal structure. However, the enhancement value of $T_c (T_{c_{RECa124}} - T_{c_{RE124}})$ decreased with increasing of RE ionic radius larger than Y. From XRD observation, the GdCa124- and SmCa124-film showed comparative large peaks originated RE123 and other phases, and we can speculate that the amount of RE / Ca substitution in RE124 phase reduced due to depriving the Ca by other phases. Therefore, it is considered that the $T_c^{RECa124} - T_c^{RE124}$ decreased with increasing of RE ionic radius larger than Y.

4. Conclusion

We fabricated the RE124- and RECa124 (amount of RE / Ca substitution: 0.1)-films by using molten hydroxide method and investigated the effect of Ca-doping in crystallization and superconducting properties. We succeeded the fabrication of RE124 and RECa124 films at low temperature (~650ºC) and the $T_c$ of YCa124 film achieved ~90 K, which is 10 K higher than that of Y124 film. Moreover, Ca-doped films of RECa124 also showed apparent $T_c$ increase about 4 ~ 10 K. The enhancement value ($T_{c_{RECa124}} - T_{c_{RE124}}$), however, were depressed on the films with larger RE ions, Gd and Sm. Obvious RE123 phase and obscure Ba-Cu-O phase were detected in the RE124-films with Gd and Sm, and RE123 phase was intensified by Ca-doping. It is speculated that the depriving of Ca by RE123 and other phases is root cause for $T_c^{RECa124} - T_c^{RE124}$ degradation of GdCa124- and SmCa124-films.

5. References

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