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## Improvement of upper critical field in $\text{YBa}_2\text{Cu}_3\text{O}_y$ films by substituting 3d metal for Cu sites using combinatorial pulsed-laser deposition

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### Abstract

It is well known that the critical upper field  $B_{c2}$  is improved by shortening of the coherence length owing to the scattering of electrons in a superconductor. In order to improve of  $B_{c2}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (YBCO) films in our study, we substituted 3d metals ( $M = \text{Zn, Co, Ni, Fe}$ ) for the Cu sites of the YBCO films. We used combinatorial pulsed-laser deposition to fabricate different  $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_y$  films by continuously changing the amount of substitution metal  $x$ , from 0 to 0.01 on a single substrate using. As a result, the superconducting transition temperature  $T_c$  and critical current density  $J_c$  decreased with increasing amounts of all four variations of substitution metal  $M$ . For example,  $T_c$  was 82.5 K and  $J_c$  at 77 K was 0.15 MA/cm<sup>2</sup> in the Co-substituted sample with  $x = 0.0091$ . For the substitution of Co and Ni, we confirmed that  $B_{c2}$  was improved with increasing amount of substitute metal up to  $x = 0.01$ . Although  $B_{c2}(0 \text{ K})$  of a pure-YBCO film was 101 T,  $B_{c2}(0 \text{ K})$  of the Co-substituted sample with  $x = 0.0091$  reached 272 T. On the other hand, the irreversibility field decreased by substituting Zn, Co, Ni, or Fe for Cu.

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**Keywords:** YBCO thin film; combinatorial pulsed-laser deposition; 3d metal; upper critical field  $B_{c2}$ .

### 1. Introduction

Using combinatorial pulsed-laser deposition (C-PLD), we can fabricate a thin film with a compositional gradient across the film. Our group has reported high-speed screening of an optimal amount of an artificial flux-pinning center (APC) and new APC materials[1]. For superconductors used in a magnetic field, such as a superconducting

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magnet, improving the upper critical field  $B_{c2}$  and the irreversibility field  $B_{irr}$ , is a very important issue. It is well known that  $B_{c2}$  is improved by shortening of the coherence length owing to the scattering of electrons in a superconductor[2]. The roles of impurity carbon atoms in  $MgB_2$ [3] and grain boundaries in  $Nb_3Sn$  wires[2] as electron scattering centers have been reported.

In this study, to improve of  $B_{c2}$  and superconducting properties at temperatures below 77 K in yttrium-barium-copper-oxide (YBCO) films, we substituted 3d metals ( $M = Zn, Co, Ni, Fe$ ) for the Cu sites in the  $YBa_2Cu_3O_y$  films. As it, has been reported that light doping with  $M$  in rare-element-barium-copper-oxide (REBCO) can turn the material into an APC[4,5], we focused primarily on the effect of  $M$  on  $B_{c2}$  as electron scattering centers in this study. Using C-PLD to fabricate different  $YBa_2(Cu_{1-x}M_x)_3O_y$  thin films by continuously changing the substitution amount  $x$  from 0 to 0.01, we explored options for the best replacement material and high-speed screening of the optimal value of  $x$ .

## 2. Experimental

The yttrium-barium-copper-3d metal-oxide [YB(CM)O] films were grown on (1 0 0)  $SrTiO_3$  substrates by C-PLD using a 4th harmonic Nd:YAG laser (wavelength : 266 nm) at a repetition rate of 2 Hz. The laser-energy density and distance between the substrate and target were  $2.0 \text{ J/cm}^2$  and 40 mm, respectively. The  $O_2$  pressure during the deposition was 40 Pa. The compositions of the bulk targets were pure  $YBa_2Cu_3O_y$  and  $YBa_2(Cu_{0.99}M_{0.01})_3O_y$  with  $M = Ni, Zn, \text{ and } Fe$ . In the case of Co substitution, we prepared a  $YBa_2(Cu_{0.98}M_{0.02})_3O_y$ -target. Post-deposition annealing was performed at 400 °C for 1 h.

The crystallinity and orientation of the thin films were evaluated by X-ray diffraction (XRD) analysis, the superconductivity was evaluated by the four-point probe method, and the amount of substitute metal in the thin films was evaluated by an energy-dispersive X-ray spectrometer attached to a scanning electron microscope (SEM-EDX). The resistivity and critical current at various magnetic field were measured by the standard four-point probe method with a physical-property measurement system (PPMS : Quantum Design). The superconducting transition temperature  $T_c$  was defined from the temperature dependence plot at a resistivity of  $0.1 \mu\Omega \text{ cm}$  and the probe current density was fixed at about  $25 \text{ A/cm}^2$ . The critical current density  $J_c$  was evaluated from the current vs. voltage curves with an electric-field criterion of  $1 \mu\text{V/cm}$ . The thickness of each film was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), which yielded a value of about 400 nm.

## 3. Results and discussion

It was confirmed by XRD that the films had biaxial orientation. Fig. 1 shows the  $x$  dependence of (a)  $T_c$  and (b)  $J_c$  at 77 K for the  $YBa_2(Cu_{1-x}M_x)_3O_y$  thin films. The value of  $T_c$  and  $J_c$  decreased monotonically with increasing  $x$  for all substitute metals. These results roughly coincide with the previous report on bulk YB(CM)O [6,7]. The reason for the  $T_c$  reduction is not clear and various hypotheses have been presented, as discussed at the end of this section.

Fig. 2 shows the temperature dependence of  $B_{c2}$  for the  $YBa_2(Cu_{1-x}M_x)_3O_y$  thin films. Here, we define  $B_{c2}(T)$  as the magnetic field and temperature at which the resistivity was 50 % of the normal-state value. In the case of Co substitution, as shown in Fig. 2 (a), it was confirmed that the slope of  $B_{c2}$  vs. temperature increases with increasing  $x$  up to about 0.01. Similarly, films in which Ni was substituted for Cu also showed the same tendency. On the other hand, in the case of Zn substitution, as shown in Fig. 2 (b), the slope of  $B_{c2}$  vs. temperature did not change much. The plots for the films in which Fe was substituted for Cu were also the same. The slope,  $|dB_{c2}/dT|$ , was improved significantly from 1.14 T/K for pure YBCO thin films to 3.11 T/K for the Co-substituted sample with  $x = 0.0091$ .

Fig. 3 shows the  $x$  dependence of  $B_{c2}(0 \text{ K})$  for the  $YBa_2(Cu_{1-x}M_x)_3O_y$  thin films. Here,  $B_{c2}(0 \text{ K})$  is defined by extrapolating the  $B_{c2}(T)$  vs.  $x$  line to 0 K. The value of  $B_{c2}(0 \text{ K})$  was greatly improved with increasing  $x$  for Co and Ni substitution. The maximum  $B_{c2}(0 \text{ K})$  value reached 272 T for the Co-substituted sample with  $x = 0.0091$ , which is about 2.7 times compared with 101 T for the pure YBCO sample.

Fig. 4 shows the  $x$  dependence of the irreversible field at 77 K,  $B_{irr}(77 \text{ K})$ , for the  $YBa_2(Cu_{1-x}M_x)_3O_y$  thin films. Here, we define  $B_{irr}(T)$  as the magnetic field and temperature where the resistivity was  $0.01 \mu\Omega \text{ cm}$ . The line shape or slope for the  $B_{irr}$  plot did not change and the value of  $B_{irr}$  decreased monotonically with increasing  $x$ ,

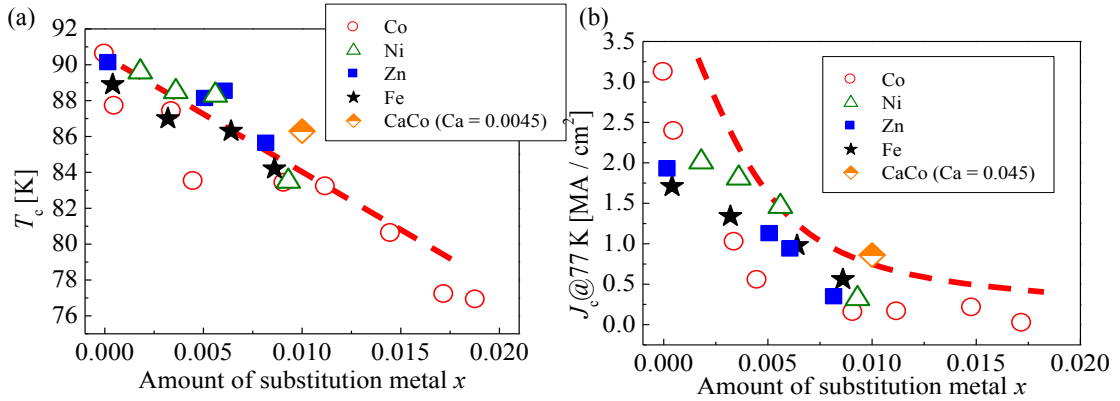


Fig. 1. Dependence of (a)  $T_c$  and (b)  $J_c$  at 77 K on  $x$  for  $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_y$  thin films.

Next, let us discuss the different  $B_{c2}(0 \text{ K})$  behavior depending on the substitute metal used. There are two types of Cu sites in YBCO that can be replaced by the 3d metals : one is in the CuO- chain, and the other is on the  $\text{CuO}_2$ -plane. The preferential substitution site depending on the type of 3d metal has been identified in sintered bulk YBCO[5,6]. However, since the growth environment of YBCO thin films is significantly different from that of bulk YBCO, the substitution site would be different from the reported sites in the bulk. Because the improvement in the  $B_{c2}$  was caused by electron scattering, it was possibility that the substitution sites of Co and Ni were on the  $\text{CuO}_2$ -plane, acting as electron-scattering centers.

The degradation of  $T_c$  and  $J_c$  was also an important issue. There have been various hypotheses why  $T_c$  decreases as a result of 3d metal substitution. The destruction of long-range order in the CuO- chain or on the  $\text{CuO}_2$ - plane by substituting a 3d metal for Cu strongly affects the breaking of the Cooper-pair or charge localization, and they lead to an under-doped state of carriers in superconductors[8]. Therefore, in order to suppress the degradation, we tried to control the carrier density in the films by doping the film with  $\text{Ca}^{2+}$ . As shown in Fig. 1,  $T_c$  and  $J_c$  of the  $\text{Ca}^{2+}$ - doped  $\text{YBa}_2(\text{Cu}_{0.990}\text{Co}_{0.010})_3\text{O}_y$  thin film were 86.3 K and 0.86 MA/cm², respectively, representing respective improvements of about 3 K and 0.7 MA/cm² compared with the non-Ca-doped  $\text{YBa}_2(\text{Cu}_{0.990}\text{Co}_{0.010})_3\text{O}_y$  sample. The value of  $B_{c2}(0 \text{ K})$  for the  $\text{Ca}^{2+}$ - doped  $\text{YBa}_2(\text{Cu}_{0.990}\text{Co}_{0.010})_3\text{O}_y$  sample was 238 T, as shown in Fig. 3, which is sufficiently high compared with the pure YBCO sample, suggested that  $T_c$  and  $J_c$  were improved while maintaining a high  $B_{c2}$  by controlling the carrier.

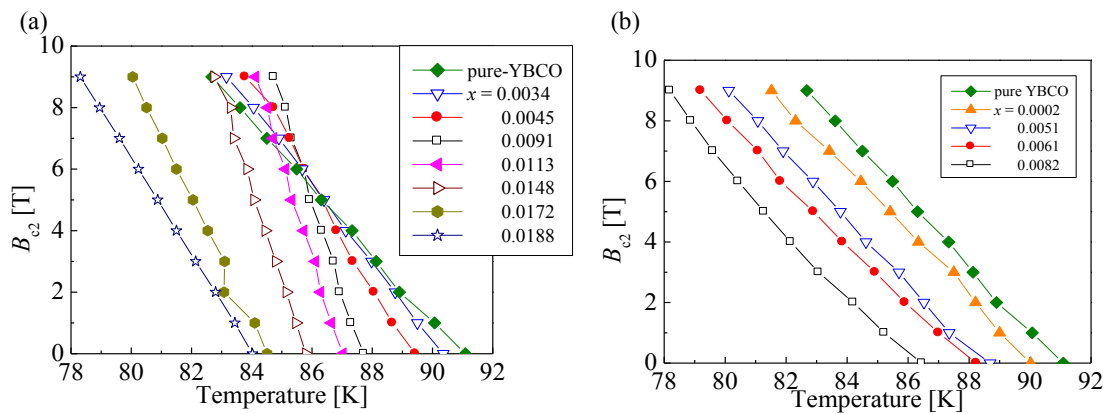


Fig. 2. Temperature dependence of  $B_{c2}$  for  $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_y$  thin films : (a)Co, (b)Zn.

#### 4. Conclusion

In this study, we substituted 3d metals ( $M = \text{Zn, Co, Ni, Fe}$ ) for the Cu sites in  $\text{YBa}_2\text{Cu}_3\text{O}_y$  films to improve the value of  $B_{c2}$ . As a result,  $B_{c2}$  increased greatly with increasing  $x$  in the Co- and Ni-substituted samples. In the Co-substituted sample with  $x = 0.0091$ ,  $B_{c2}(0 \text{ K})$  was 272 T, which was 2.7 times higher than the value for the pure YBCO sample. On the other hand,  $T_c$  and  $J_c$  decreased with increasing  $x$  regardless of the substitution element. The improvement of  $T_c$  and  $J_c$  reduction and as well as clarification of the reason for the  $B_{c2}$  improvement depending on the substitution element are challenging issues in future studies of YBCO superconducting films.

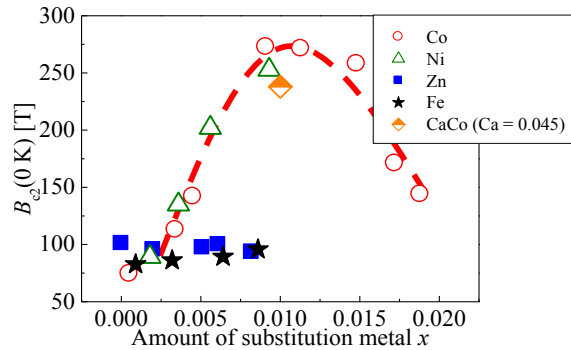


Fig. 3. Dependence of  $B_{c2}(0 \text{ K})$  on  $x$  for  $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_y$  thin films.

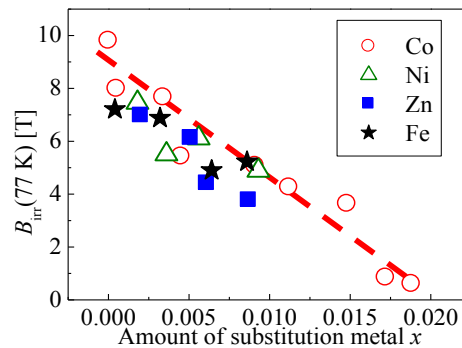


Fig. 4. Dependence of  $B_{irr}(77 \text{ K})$  on  $x$  for  $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_y$  thin films.

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