Fabrication of high-entropy REBa$_2$Cu$_3$O$_{7-\delta}$ thin films by pulsed laser deposition

Aichi Yamashita$^{1,*}$, Kazuki Hashimoto$^1$, Shunta Suzuki$^1$, Yusuke Nakanishi$^1$, Yasumitsu Miyata$^1$, Toshihiko Maeda$^{2,3}$, and Yoshikazu Mizuguchi$^1$

$^1$Department of Physics, Tokyo Metropolitan University, Hachioji 192-0397, Japan
$^2$School of Environmental Science and Engineering, Kochi University of Technology, Kami 782-8502, Japan
$^3$Center for Nanotechnology, Kochi University of Technology, Kami 782-8502, Japan

E-mail: aichi@tmu.ac.jp

Received February 12, 2022; accepted March 6, 2022; published online May 18, 2022

Supplementary material for this article is available online

Thin films of REBa$_2$Cu$_3$O$_{7-\delta}$ (RE123, RE: rare earth) having a high-entropy (HE) RE site were successfully fabricated by the pulsed laser deposition method. Solution various RE elements result in increasing configurational entropy of mixing. Current critical density of the HE films exceeds an order of 1.0 MA cm$^{-2}$ under conditions of $T < 20$ K and $\mu_0 H < 7$ T. Since the HE effects have a potential to an improvement of irradiation tolerance, the present results encourage further development of HE RE123 superconducting materials used in the environment with high magnetic fields and irradiation, for example in fusion reactors. © 2022 The Japan Society of Applied Physics

Since the discovery of high-transition-temperature (high-$T_c$) cuprate superconductor, various kinds of cuprate superconductors have been reported. Among them, REBa$_2$Cu$_3$O$_{7-\delta}$ (RE123, RE: rare earth) is a promising material for high-field superconductivity application because of its high-$T_c$ and high critical current density (high-$J_c$) under magnetic fields in a thin film form. These characteristics enable us to practically use RE123 superconductors under high temperatures and high magnetic fields, which are not capable by low-$T_c$ superconductors such as NbTi and Nb$_3$Sn. High-$T_c$ cuprate superconductors are desired as a promising candidate for a magnet material in a next-generation energy reactor, because of their high critical magnetic field more than 20 T could realize the compact nuclear fusion design and operating at relatively high temperature such as $T = 20$ K, which are not possible by low-$T_c$ superconductors. In a nuclear fusion reaction, neutrons are generated and irradiate surrounding superconducting magnets. In some practical superconductors such as Nb$_3$Sn and REBa$_2$Cu$_3$O$_{7-\delta}$, it has been revealed that the superconducting characteristics obviously deteriorate by neutron and high-energy particle irradiation. Therefore, development of superconducting material sufficiently resistant to the environment under high-energy particle irradiation is one of the most important issues for the safe operation of the next-generation energy reactor.

Recently, an excellent irradiation resistance has been reported in CoCrFeMnNi$^{16-18}$ which is so-called high-entropy alloys (HEAs). HEAs are typically defined as alloys containing at least five elements with concentrations between 5% and 35%.$^{14,15}$ HEAs have high configurational mixing entropy ($\Delta S_{\text{mix}}$), defined as $\Delta S_{\text{mix}} = -R \Sigma c_i \ln c_i$, where $c_i$ and $R$ are the compositional ratio and the gas constant, respectively.$^{14,15}$ HEAs have recently attracted much attention in the fields of materials science and engineering because they exhibit excellent performance under extreme conditions.$^{15,16}$ Even though the reason for its excellent irradiation resistance is still unclear, the atomic-level stress and local lattice distortions in the CoCrFeMnNi HEA have been believed to increase the migration barrier of point defects induced by irradiation.$^{10}$ These findings make the HEA material as a promising candidate in a high-energy particle irradiation environment.

Furthermore, the discovery of a HEA superconductor of Ti–Zr–Ho–Nb–Ta in 2014 by Koželj et al. triggered the development of HEA superconductors.$^{16}$ Since 2018, we have developed HEA-type superconducting compounds, in which the HEA concept was extended to complicated compounds having two or more crystallographic sites.$^{18}$ Comparing the effects of HEA states on superconductors with various crystal structural dimensionality, we found that the disordering effects introduced by the HEA-type site in Bi$_2$Sr$_2$CuO$_6$-based layered system$^{19}$ and tetragonal Tr$_2$Zr$_2$ (Tr: transition metals) quasi-two-dimensional system$^{20-22}$ does not suppress its original $T_c$ in pure phases. These findings suggest that the HEA effects in layered superconductors seem to work positively or at least less negatively. We also previously reported the synthesis of HEA-type RE123 poly-crystalline samples and reported that the increase in $\Delta S_{\text{mix}}$ does not suppress superconducting properties including $J_c$ (global)$^{23}$ and possible improvement of intra-grain $J_c$ ($J_{\text{local}}$) for RE123 using lighter RE elements including Dy, Ho.$^{24}$ These background knowledges have motivated us to study superconducting properties of high-entropy (HE) RE123 thin films. In this letter, we show the successful fabrication of the thin film of RE123 on a SrTiO$_3$ substrate with various $\Delta S_{\text{mix}}$ at the RE site. To the best of our knowledge, this is the first report on fabrication of a HEA-type superconducting thin film. Although the $J_c$ of some films with more than three RE elements was slightly lower than that of pristine one, we found that all films exhibited the $J_c$ values over an order of 1.0 MA cm$^{-2}$ under conditions of $T < 20$ K and $\mu_0 H < 7$ T. These results revealed a potential for the practical use of HE RE123 superconducting films, for example in the next-generation energy reactor.

All thin film samples were fabricated at 920 °C by a pulsed laser deposition (PLD) method with a 266 nm Nd:YAG laser and frequency of 4 Hz with a laser energy density of around 1.3 J cm$^{-2}$. An oxygen pressure was kept at 1.0 × 10$^4$ Pa during the deposition, and then kept at 2.0 × 10$^4$ Pa during cool down to room temperature at a rate of 5 °C min$^{-1}$. Targets of REBa$_2$Cu$_3$O$_{7-\delta}$ (RE: Y, Sm, Eu, Dy, Ho) were prepared by the conventional solid state reaction in air as described in Refs. 23 and 24.

The films were grown on a SrTiO$_3$ (STO) (001) substrate. Distance between the target and substrate was 33.5 mm. X-ray diffraction (XRD) patterns...
were collected on a MiniFlex-600 diffractometer (RIGAKU), equipped with a D/tex-Ultra high-resolution detector, with a Cu–Kα radiation by a conventional \( \theta-2\theta \) method. The actual composition of the synthesized thin films were investigated by X-ray fluorescence (XRF) spectrum was recorded using JSX-1000S (JEOL) with the Rh target. The obtained compositions are listed in Table I. Thickness of the obtained films were estimated by Atomic Force Microscopy (AFM, Park System NX10) in a non-contact scanning mode. The superconducting properties were investigated using a superconducting quantum interference device (SQUID) magnetometer on MPMS-3 (Quantum Design). The temperature dependence of magnetization was measured after both zero-field cooling (ZFC) and field cooling (FC) with an applied field of 10 Oe. The electrical resistivity was measured on a GM refrigerator system (Made by Axis) by the four-probe method from room temperature to 70 K. The four Au electrodes were deposited on the obtained thin films by vacuum deposition with a shadow mask and Au wires were connected to the electrodes with a silver paste. According to the number of RE elements solved in the RE site, examined samples are labeled \( \text{RE}1-\text{RE}5 \) (see Table I). Figure 1(a)  

### Table I. Compositional, configurational mixing entropy (\( \Delta S_{\text{mix}} \)), and superconductivity, thickness of \( \text{REBa}_2\text{Cu}_3\text{O}_{7-\delta} \) thin films.

| RE composition | \( \Delta S_{\text{mix}}/R \) | \( T_c^{\text{onset}} \) (K) | \( T_c^{\text{zero}} \) (K) | \( T_c^{\text{mag}} \) (K) | \( J_c \) (MA cm\(^{-2}\)) | \( t \) (nm) |
|----------------|----------------|----------------|----------------|----------------|----------------|---------|
| Y | 0 | 91.5 | 88.0 | 86.0 | 11.5 | 220 |
| \( \text{Y}_{0.16}\text{Sm}_{0.33}\text{Eu}_{0.52} \) | 1.00 | 90.5 | 88.6 | 87.5 | 4.3 | 255 |
| \( \text{Y}_{0.11}\text{Sm}_{0.14}\text{Eu}_{0.49}\text{Dy}_{0.26} \) | 1.22 | 90.5 | 86.0 | 87.8 | 7.5 | 181 |
| \( \text{Y}_{0.12}\text{Sm}_{0.08}\text{Eu}_{0.26}\text{Dy}_{0.18}\text{Ho}_{0.36} \) | 1.48 | 90.5 | 85.0 | 87.0 | 6.5 | 208 |

Fig. 1. (Color online) (a) X-ray \( \theta-2\theta \) scan patterns of the obtained \( \text{REBa}_2\text{Cu}_3\text{O}_{7-\delta} \) thin films for \( \text{RE}1 \) to \( \text{RE}5 \) grown on \( \text{STO}_3 \) \((0 0 1)\) with the X-ray intensity on a logarithmic scale and (b) enlarged figure around \( \text{RE}123 \) \((0 0 5)\). (c) Lattice constant \( c \) against the number of RE element.
shows an X-ray $\theta - 2\theta$ scan patterns of the obtained thin films for RE1 to RE5 grown on the STO (0 0 1) substrate. Except for the diffraction peak from the STO substrate, only (0 0 l) diffraction peaks of RE123 are observed, indicating the single phase and the c-axis oriented growth of obtained thin films. Slight broadening of the (0 0 l) diffraction peaks was observed [Fig. 1(b)] for films with a larger number of RE elements, while no peak split was seen by laboratory XRD. Figure 1(c) shows the lattice constant $c$ against the number of RE element. Increase of lattice constant $c$ was observed with increase of number of RE element. Larger lattice constant $c$ compared to that of RE1 is possibly due to the inclusion of larger ionic radius RE element than RE = Y. Since several RE elements with different ionic radius are supposed to be mixed in RE site, various lattice distortions such as lattice mismatch and influence from the substrate caused by mixing and lattice defects such as anti-phase boundaries might occur in present films. To reveal these situation, further experiment regarding the lattice mismatches and so on are required. The estimated compositions of RE element by XRF analysis is summarized together with $\Delta S_{\text{mix}}$ value in Table 1. The fabricated film of RE5 have $\Delta S_{\text{mix}}$ of 1.5 $R$, which is a typical value of HEAs, is same as that of HEAs and enough to examine the effect of entropy to superconducting properties of the RE123 films.

Fig. 2. (Color online) (a) Temperature dependence of magnetization for the obtained REBa$_2$Cu$_3$O$_{7-\delta}$ thin films for RE1 to RE5 and (b) enlarged figure of ZFC around the $T_c$. (c) Magnetic field dependences of magnetic $J_c$ at $T = 4.2$ K estimated using Bean’s model.

Fig. 3. (Color online) (a) Temperature dependence of electrical resistivity for the obtained REBa$_2$Cu$_3$O$_{7-\delta}$ thin films for RE1 to RE5 and (b) enlarged figure around the $T_c$. 

050905-3 © 2022 The Japan Society of Applied Physics
Figure 2(a) shows the temperature dependence of magnetization for RE$_1$–RE$_5$ and the Fig. 2(b) is the enlarged figure around $T_c$. Large diamagnetic signals corresponding to the superconductivity are observed at around 87 K for all samples. Slightly lower $T_c$ of obtained samples as compared to those of previously reported bulk samples$^{24}$) would be related to the oxygen amount condition during growth and/or cooling to room temperature. The bulk nature of superconductivity of obtained samples were confirmed through the $M$–$T$ measurements and magnetization-magnetic field ($M$–$H$) loops in Fig. 4. Although a HE thin film exhibited same $T_c$ as pristine one, broadening of transition below $T_c^{\text{mag}}$ was observed in RE3–RE5 samples. The slight broadening of transition is also observed in some HEA-type compound superconductors.$^{22,25}$ From the specific heat measurement of those superconductors, broadening of superconducting transition jump was found, indicating that the observed broadening of magnetization transition would be related to similar origins. To reveal the origin of these phenomena, further experiments which can directly observe the superconducting gap structure, such as scanning tunneling microscopy (STM) or Angle-resolved photoemission spectroscopy (ARPES) measurement are desired. In that sense, the successful fabrication of thin film is a meaningful achievement for such investigations. Temperature dependence of resistivity for all films are plotted in Fig. 3(a) with enlarged figure around $T_c$ [Fig. 3(b)]. All films exhibited metallic behavior from room temperature down to the superconducting transition temperature. Superconducting transition temperature of $T_c^{\text{onset}}$ and $T_c^{\text{zero}}$ were summarized in Table I. The transition width ($\Delta T_c$) of obtained films was 3.5, 1.9, 4.5 and 5.5 for RE1, RE3, RE4 and RE5, respectively. Slightly larger $\Delta T_c$ in the HE films, which possibly due to the introduction of strain by HE, is consistent with the slight broadening of transition in magnetization measurement.

To estimate $J_c$ of the thin films, $M$–$H$ loops were measured. From the obtained $M$–$H$ loops, $J_c$ was estimated using the Bean’s model$^{26}$: 

$$J_c = 20\Delta M / b (1 - b/3a) (\text{A cm}^{-2})$$

where $a$ and $b$ are lengths determined by sample shape, and $\Delta M$ is obtained from the width of the $M$–$H$ curve. The typical results on $J_c$ at $T = 4.2$ K are plotted as a function of magnetic field in Fig. 3(c). At lower magnetic fields, the difference of $J_c$ between the samples with zero to high entropy are clear, while the difference becomes smaller in higher magnetic fields except for RE3. In particular, the $J_c$ of RE4 and RE5 closed to that of RE1 above $\mu_0 H = 2.0$ T. As

![Fig. 4.](https://example.com/figure.png)
shown in Fig. S1 (available online at stacks.iop.org/JIAP/61/050905/mmedia) (see the supplementary material), $J_c$ against number of $RE$ at low-magnetic-field region shows a similar trend with previously reported $J_c$ values in polycrystalline samples.\(^{24}\) $M$–$H$ loop and $J_c$ at $T = 2.0$, 4.2, 10.0, 20.0, 50.0, 77.3, 90.0, 100.0 K for $RE$–$RE$ are plotted in Figs. 4(a)–4(h). Although $J_c$ of $RE$–$RE$ slightly decreases compared to that of $RE1$ at low magnetic fields, the $J_c$ values of the $RE4$ and $RE5$ films recorded approximately 2.4 and 2.3 MA cm$^{-2}$ at $T = 4.2$ K under around $\mu_0 H = 7$ T. In addition, their $J_c$ also exceed an order of 1.0 MA cm$^{-2}$ up to 20 K in entire fields. We emphasize that the finding that the increase of $\Delta S_{mix}$ does not significantly deteriorate the $J_c$ should be quite positive because HE effects are expected to improve functionality other than superconducting properties. As described earlier, the improvement of irradiation resistance is one of the most important tasks for the practical use of high-$T_c$ superconductors in a fusion reactor. Therefore, our current results will encourage further studies on HE $RE123$ materials from the perspective of possible achievement of both high-$J_c$ and excellent irradiation tolerance. Moreover, it is well known that an enhancement of $J_c$ is usually achieved by combining with introduction of artificial pinning center (APC) such as BaZrO$_3$.\(^{25-29}\) Since the present samples are not optimized with any APCs, there should be more space for further improvement of $J_c$ in HE $RE123$ films. Further investigation on film fabrication process, superconducting properties, and irradiation tolerance is required to clarify the irradiation resistance of HE $RE123$ superconductors and for further development of superconducting application field.

In conclusion, we reported the successful fabrication of high-entropy $RE$Ba$_2$Cu$_3$O$_{7-\delta}$ ($RE123$, $RE$: rare earth) thin films on the SrTiO$_3$ substrate by a pulsed laser deposition method. Observation of only (0 0 1) diffraction peaks of $RE123$ except for substrate indicates the single phase and the $c$-axis oriented growth of obtained thin films. SEM-EDX analyses revealed that there is no compositional segregation in all films and confirmed different configurational entropy of mixing at the $RE$ site. From the characterizations of superconducting properties, the $J_c$ of the $RE4$ and $RE5$ films are estimated as approximately 2.4 and 2.3 MA cm$^{-2}$ at 4.2 K under around 7 T and exceeded an order of 1.0 MA cm$^{-2}$ up to 20 K in entire fields. In addition, their $J_c$ becomes comparable to that of $RE1$ under high-field region. Since the increase of $\Delta S_{mix}$ does not deteriorate the $J_c$ significantly in HE $RE123$ films, this material will be useful for application under high fields and irradiation like a next-generation fusion reactor, after improvement of irradiation tolerance.

Acknowledgments The authors thank T. Nakano, O. Miura, Y. Shukunami, and Y. Goto for support in experiments and discussion. This work was partly supported by JSPS-KAKENHI (18KK0076, 21H00151) and Tokyo Metropolitan Government Advanced Research (H31-1) Iketani Science and Technology Foundation.

References

1) J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter 64, 189 (1986).
2) M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. 58, 908 (1987).
3) H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. 27, L209 (1988).
4) A. Schilling, M. Cantioni, J. D. Guio, and H. R. Ott, Nature 363, 56 (1993).
5) C. W. Chu, L. Z. Deng, and B. Lv, Physica C 514, 290 (2015).
6) T. S. S. Oh, H. S. Kim, H. S. Ha, R. K. Ko, D. W. Ha, H. Lee, S. H. Moon, and S. J. Yoo, Supercond. CRYOG. 15, 1 (2013).
7) P. Bruzzone, W. H. Fietz, J. V. Minervini, M. Novikov, N. Yanagi, Y. Zhai, and J. Zheng, Nucl. Fusion 58, 103001 (2018).
8) V. Bartítková, J. L. Pérez-Diaz, T. Hlásek, L. Vieretl, and H. A. Vratislavský, Ceram. Int. 46, 15400 (2020).
9) T. A. V. Troitskii, T. E. Demikhov, L. Kh. Antonova, A. Yu. Dudyk, and G. N. Mikhailova, J. Surf. Invest. 10, 381 (2016).
10) Q. Xu, H. Q. Guan, Z. H. Zhong, S. S. Huang, and J. J. Zhao, Sci. Rep. 11, 608 (2021).
11) K. Jin, C. Lu, L. M. Wang, J. Q. Wu, W. J. Weber, Y. Zhang, and H. Bei, Scr. Mater. 119, 65 (2016).
12) L. Yang et al., J. Mater. Sci. Technol. 35, 300 (2019).
13) X. L. Ren, B. D. Yao, T. Zhu, Z. H. Zhong, Y. X. Wang, X. Z. Cao, S. Jinno, and Q. Xu, Intermetallics 126, 106942 (2020).
14) J. W. Yeh, S. K. Chen, S. J. Lin, Y. J. Gan, T. S. Chin, T. T. Shun, C. H. Tsau, and S. Y. Chang, Adv. Eng. Mater. 6, 299 (2004).
15) M. H. Tsai and J. W. Yeh, Mater. Res. Lett. 2, 107 (2014).
16) A. O. Moghaddam and E. A. Troilmø, J. Alloys Compd. 851, 156838 (2020).
17) P. Koželj, S. Vrtnik, A. Jelen, S. Jazbec, Z. Jagličič, S. Maiti, M. Feuerbacher, W. Steurer, and J. Dolinšek, Phys, Rev. Lett. 113, 107001 (2014).
18) Y. Mizuguchi and A. Yamashita, “Advances in High-Entropy Alloys - Materials Research, Exotic Properties and Applications,” IntechOpen, Chapter 1.
19) R. Sagabe, Y. Goto, and Y. Mizuguchi, Appl. Phys. Express 11, 053102 (2018).
20) Y. Mizuguchi, M. R. Kasem, and T. D. Matsuda, Mater. Res. Lett. 9, 141 (2021).
21) M. R. Kasem, A. Yamashita, Y. Goto, T. D. Matsuda, and Y. Mizuguchi, J. Mater. Sci. 56, 9499 (2021).
22) M. R. Kasem, A. Yamashita, T. Hatano, K. Sakurai, N. Oono-Hori, Y. Goto, O. Miura, and Y. Mizuguchi, Supercond. Sci. Technol. 34, 125001 (2021).
23) Y. Shukunami, A. Yamashita, Y. Goto, and Y. Mizuguchi, Physica C 572, 135623 (2020).
24) A. Yamashita, Y. Shukunami, and Y. Mizuguchi, Accepted in R. Soc. Open Sci., arXiv:2103.12261.
25) A. Yamashita, T. D. Matsuda, and Y. Mizuguchi, J. Alloy Compd. 686, 159233 (2021).
26) C. P. Bean, Rev. Mod. Phys. 36, 31 (1964).
27) P. Patuir, M. Malmivirta, H. Palonen, and H. Huhtinen, J. Phys.: Conf. Ser. 507, 012040 (2014).
28) A. Augieri et al., J. Appl. Phys. 108, 063906 (2010).
29) A. Augieri et al., IEEE Trans. Appl. Supercond. 19, 3399 (2009).