



 Cite this: *RSC Adv.*, 2023, **13**, 17253

## Effect of Er/Y addition on the growth and superconductivity of Bi2212 films

 Bowen Zhang<sup>a</sup> and Yang Qi <sup>\*ab</sup>

In order to increase the critical current density of Bi2212 superconducting films to broaden their application areas. A series of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta-x}\text{RE}_2\text{O}_3$  (RE = Er/Y) ( $x = 0, 0.04, 0.08, 0.12, 0.16, 0.20$ ) thin films were prepared by the sol–gel method. The structure, morphology and superconductivity of the  $\text{RE}_2\text{O}_3$  doping films were characterized in detail. The effect of  $\text{RE}_2\text{O}_3$  on the superconductivity of Bi2212 superconducting films was investigated. It was shown that the Bi2212 films were (00 $l$ ) epitaxially grown. The in-plane orientation relationship between the Bi2212– $x\text{RE}_2\text{O}_3$  and the  $\text{SrTiO}_3$  was Bi2212[100](001)// $\text{SrTiO}_3$ [011](100). The grain size in the out-of-plane direction of Bi2212 tends to increase with the amount of  $\text{RE}_2\text{O}_3$  doping. Doping with  $\text{RE}_2\text{O}_3$  had no significant effect on the anisotropy of Bi2212 crystal growth, but inhibited the agglomerative growth of the precipitated phase on the surface to a certain extent. Furthermore, the conclusion was that the superconducting transition temperature ( $T_{\text{c,onset}}$ ) was almost unaffected, while the zero resistance transition temperature ( $T_{\text{c,zero}}$ ) continued to decrease with increasing doping level. The thin film samples Er2 ( $x = 0.04$ ) and Y3 ( $x = 0.08$ ) exhibited the best current-carrying capacity in magnetic fields.

Received 11th April 2023

Accepted 1st June 2023

DOI: 10.1039/d3ra02397d

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### Introduction

Since the discovery of bismuth-based high-temperature superconducting materials (HTSC), researchers have attempted to modify their structures through various techniques to improve the magnetic and superconducting properties of superconducting materials.<sup>1–4</sup> Bi2212 has been widely studied for its small power loss, high current, magnetic field carrying capacity, electronic properties, and structural properties. However, the application of Bi-based superconductors has significant limitations in terms of critical current density, such as weak integration and weak flux pinning.<sup>5</sup> The replacement of elements in Bi-based superconductors and the addition of second-phase substances have been shown to be an effective means of improving their superconductivity and magnetic properties. These works have been extensively investigated.<sup>6–9</sup> In this case, the trend of the superconducting properties is closely related to the properties of the dopant in the crystal structure.<sup>5</sup> The phase structure and physical properties of Bi2212 superconductors can be modified by replacing or adding elements with different ionic radii or different binding properties.

Rare earth elements exhibit special physical and chemical properties in the fields of optics, electricity and magnetism due to their unique electronic structure. Rare earth metals and their

compounds have good applications. Rare earth elements play an important role in almost all high-temperature superconducting materials. For example, the addition of  $\text{Sm}_2\text{O}_3$  nanoparticles improved electrical transport properties of Bi2223 at very low doping levels.<sup>10</sup> The addition of small amounts of Nb improved the Bi2223 grain boundary connectivity, resulting in better superconductivity of the BSCCO system.<sup>11</sup> In addition, the substitution of rare earth ions is an effective means to improve the superconducting transition temperature and critical current density by adjusting the phase structure and microstructure.<sup>12–15</sup> Besides, rare earth elements are also widely used in the REBCO family. Substitution of Y by RE elements can improve their superconductivity properties in different ways, such as lower processing temperature and wider processing window for smaller RE ions<sup>16,17</sup> and higher critical transition temperature for larger RE ions.<sup>18,19</sup>

The main factors that reduce the critical current density of HTSC are grain boundaries and poor flux pinning.<sup>20</sup> Low values of critical current density at grain boundaries in polycrystalline samples are an important issue for high current applications, for which increasing the critical current density is a key issue. The nanoscale superconductivity has attracted much attention during the past decades.<sup>21–23</sup> The presence of flux pinning centers in non-ideal class II superconductors due to crystal structure defects will greatly increase their current-carrying capacity in both self-magnetic fields and external magnetic fields, making high-temperature superconductors extremely promising for applications in the strong direction. The property led scientists to search for forms of high-temperature

<sup>a</sup>Department of Materials Physics and Chemistry, School of Materials Science and Engineering, State Key Laboratory of Rolling and Automation, Northeastern University, Shenyang, Liaoning 110819, PR China. E-mail: qiyang@imp.neu.edu.cn

<sup>b</sup>Key Laboratory for Anisotropy and Texture of Materials, Ministry of Education, Northeastern University, Shenyang, 110819, P. R. China



superconductors with stronger current-carrying capacity by artificially designing the shape, density and distribution of pinning centers.<sup>24–27</sup> Related studies have shown that the nanoscale second phase has superior properties  $J_c$  values as a pinning center for superconductors. In contrast, the effect of doping of Er and Y elements on Bi2212 has rarely been investigated.

We have conducted extensive studies on the preparation of Bi2212 superconducting films by sol-gel method with aqueous solvents.<sup>28–31</sup> It was shown that this environmentally friendly and low-cost method can prepare high quality Bi2212 superconducting films. At the same time, the sol-gel method can maintain homogeneity at the atomic level. Therefore, the method offers irreplaceable advantages for the preparation of highly dispersive doped Bi2212 samples as well.

In this chapter, Bi2212 superconducting films with different RE (RE = Er/Y) doping amounts were prepared on SrTiO<sub>3</sub>(100) substrates using the sol-gel method. To investigate the optimal conditions for RE<sub>2</sub>O<sub>3</sub> doping of Bi2212 superconducting films. And to explore its effects on the crystallographic properties, surface morphology and electrical transport properties of Bi2212 superconducting films.

## Experimental

In this chapter, Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+δ</sub>-xRE<sub>2</sub>O<sub>3</sub> (Bi2212-xRE<sub>2</sub>O<sub>3</sub>) (RE = Er/Y) ( $x = 0, 0.02, 0.04, 0.06, 0.08, 0.10$ ) superconducting films were prepared by the sol-gel method. The analytical reagents Bi(NO<sub>3</sub>)<sub>3</sub>-5H<sub>2</sub>O, Sr(NO<sub>3</sub>)<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>-4H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>-3H<sub>2</sub>O, Er(NO<sub>3</sub>)<sub>3</sub>-6H<sub>2</sub>O and Y(NO<sub>3</sub>)<sub>3</sub>-6H<sub>2</sub>O were used as reactants in the molar ratio Bi : Sr : Ca : Cu = 2 : 2 : 1 : 2. Glycine was used as complexing agent and deionized water was used as solvent. The blue colored sol was obtained after stirring. 2 mL of nitric acid was added to the Bi2212 sol to maintain an acidic environment and made the sol more stable. 5 wt% PVP solution was added to give a concentration of  $c(\text{PVP}) = 0.5$  wt%. The 0.5 wt% PVP in the sol was more favorable for the sol to form a thin film by the spin coating method.

After coating the sol-gel films on the SrTiO<sub>3</sub>(100) substrate, the precursor films were heated at 413 K for 40 min to form the precursor films. To obtain a certain thickness of sample, this

process was repeated three times. The samples were then heat treated in the tube furnace with a sintering temperature of 1098 K and a holding time of 35 min to form the final Bi2212 films. The Bi2212-xEr<sub>2</sub>O<sub>3</sub> samples were named as the Er group, named Er1–Er6 in that order. The Bi2212-xY<sub>2</sub>O<sub>3</sub> samples were named as the Y group and named as Y1–Y6 in order. All the samples were sintered at 1098 K with a holding time of 35 min.

The phase composition and crystallinity of the superconducting films were characterized by a Rigaku-Smart Lab X-ray diffractometer (Cu-K $\alpha$  radiation). The  $\theta$ - $2\theta$  scan range was 3°–50°, with a scan step of 0.02° and a scan speed of 1° min<sup>-1</sup>. The Phy scan and swing curves of the films were characterized by a Smartlab(3) X-ray diffractometer (Cu-K $\alpha$  radiation). The surface morphology of the Bi2212 superconducting films was observed by field emission scanning electron microscopy (FESEM) (Zeiss). The surface structure was further investigated by atomic force microscopy (AFM) (Nanoscan Easy2) and the surface roughness of the samples was counted, using a non-contact tap mode. X-ray photoelectron spectroscopy (XPS) was obtained using a Kratos-Axis Supra from Shimadzu Corporation, Japan. X-ray photoelectron spectrometer. The superconducting properties of the samples were measured by the standard four-probe method. The Physical Property Measurement System (PPMS) measures in the temperature range of 2–300 K and in the magnetic fields range of 0–9 T.

## Results and discussion

The crystallographic properties of the samples were characterized by XRD. As shown in Fig. 1, Fig. 1(a) showed the XRD pattern of the Er1–Er6 samples and Fig. 1(b) showed the XRD pattern of the Y1–Y6 samples. The detailed crystallographic information was shown in Table 1. As can be seen in Fig. 1(a) and (b), only the diffraction peak of Bi2212(00 $l$ ) can be observed in all samples, indicating that the prepared thin film samples were all grown in  $c$ -axis selective orientation. The diffraction peaks near 5.750°, 17.308°, 23.147°, 29.048° and 35.028° correspond to the (002), (006), (008), (0010) and (0012) crystal planes of Bi2212 (PDF 79-2183), respectively. The rest of the diffraction peaks in Fig. 1(a) were all SrTiO<sub>3</sub> diffraction peaks

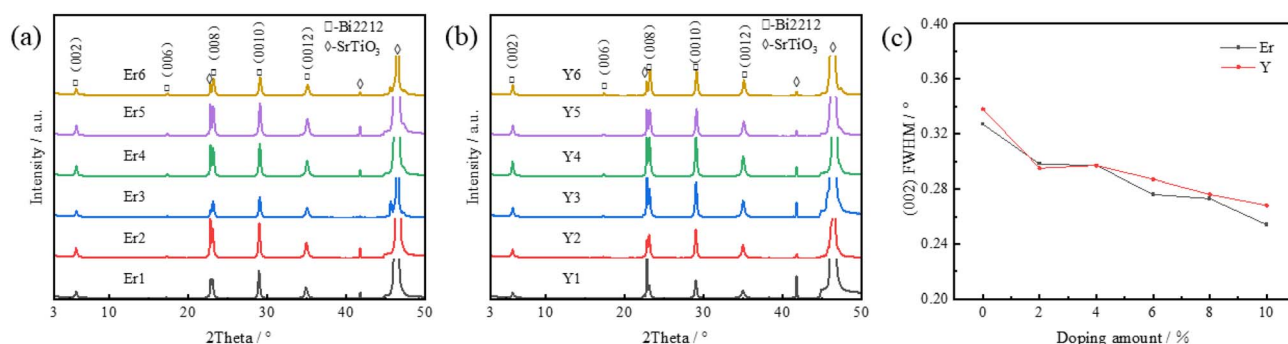


Fig. 1 XRD patterns of the samples. (a) XRD patterns of samples Er1–Er6. (b) XRD patterns of samples Y1–Y6. (c) FWHM variation of RE-doped Bi2212 superconducting films.

Table 1 Crystallographic properties of samples

Sample	Doping amount/%	(002) peak position/ $^{\circ}$	$X_{\text{Bi2212}}/\%$	(002) FWHM/ $^{\circ}$	Grain size/nm	Rms/nm
Er1	0.00	5.79	97.1	0.33	26.2	12.2
Er2	0.04	5.77	98.3	0.30	29.6	11.9
Er3	0.08	5.81	95.8	0.30	28.2	17.3
Er4	0.12	5.81	95.8	0.28	29.2	11.4
Er5	0.16	5.81	95.7	0.27	31.1	11.0
Er6	0.20	5.81	95.9	0.25	31.5	10.9
Y1	0.00	5.79	97.2	0.34	24.9	9.6
Y2	0.04	5.79	97.2	0.30	28.4	11.1
Y3	0.08	5.79	96.9	0.30	27.6	12.1
Y4	0.12	5.79	97.0	0.29	30.5	14.7
Y5	0.16	5.81	95.8	0.28	32.9	15.3
Y6	0.20	5.81	95.7	0.27	33.5	13.1

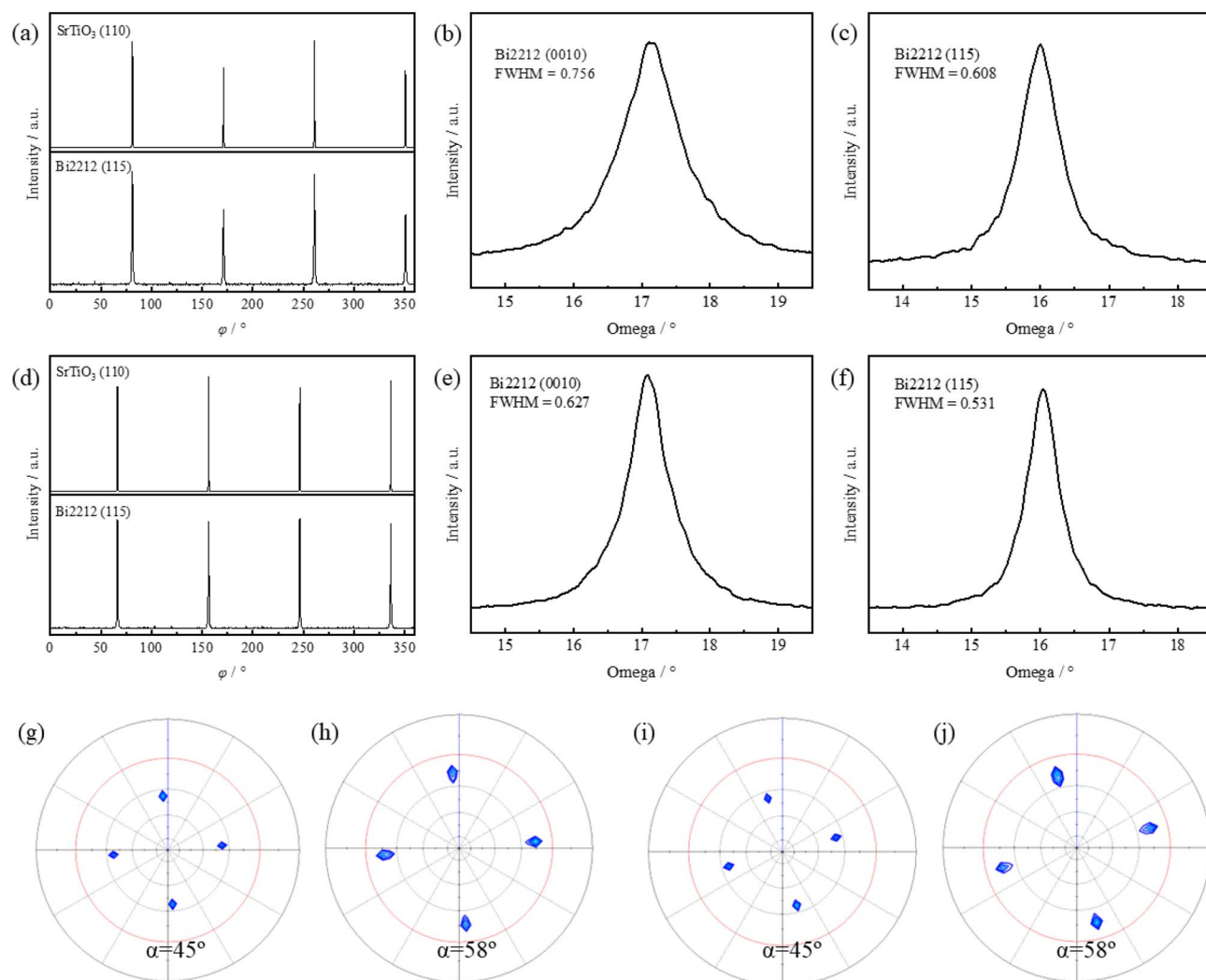


Fig. 2 (a) Phi scan XRD scans of the Bi2212(115) and SrTiO<sub>3</sub>(110) surfaces of sample Er6. (b)  $\omega$  scan XRD pattern of the Bi2212(0010) of sample Er6. (c)  $\omega$  scan XRD pattern of the Bi2212(115) of sample Er6. (d) Phi scan XRD scans of the Bi2212(115) and SrTiO<sub>3</sub>(110) surfaces of sample Y6. (e)  $\omega$  scan XRD pattern of the Bi2212(0010) of sample Y6. (f)  $\omega$  scan XRD pattern of the Bi2212(115) of sample Y6. (g) X-rays pole figures for SrTiO<sub>3</sub>(110) plane of Er-6. (h) X-rays pole figures for Bi2212(115) plane of Er6. (i) X-rays pole figures for SrTiO<sub>3</sub>(110) plane of Y-6. (j) X-rays pole figures for Bi2212(115) plane of Y6.



and the rest of the diffraction peaks in Fig. 1(b) were also SrTiO<sub>3</sub> diffraction peaks. We found that the diffraction peak of Bi2212 was shifted towards a high angle. This was due to the presence of the intergrowth phase (Bi2212<sub>x</sub>Bi2201<sub>1-x</sub>) in Bi2212. Therefore, we need to calculate the purity of Bi2212 in the samples as in eqn (1).<sup>32,33</sup>

$$X_{\text{Bi2212}} = (\theta_{\text{Bi2201}} - \theta) / (\theta_{\text{Bi2212}} - \theta_{\text{Bi2201}}) \quad (1)$$

where  $\theta$ ,  $\theta_{\text{Bi2201}}$  and  $\theta_{\text{Bi2212}}$  are the diffraction peak position of intergrowth phase, the pure Bi2201 phase (002) crystal plane (PDF 79-2181) and the pure Bi2212 phase (002) crystal plane, respectively. The calculated results were shown in Table 1. The purity of the Bi2212 phase in the films were all above 95%. The crystallinity of the samples was good and their grain size was calculated by the Scherrer formula,<sup>34</sup> the results were shown in Table 1. The RE<sub>2</sub>O<sub>3</sub> diffraction peaks could not be observed in the XRD pattern due to the low doping amount. This may be due to poor crystallinity and less content.

In order to further analyze the crystallinity of the samples, the half-height widths (FWHM) and grain sizes were counted and the information was shown in Table 1. The grain sizes were calculated from the Scherrer formula. The results showed that the Bi2212 sample had good crystallinity and there was an increasing trend of grain size with increasing RE<sub>2</sub>O<sub>3</sub> doping in the out-of-plane direction of the sample, as shown in Fig. 1(c).

This may be due to the addition of the second phase reducing the microstrain in the film matrix. It resulted an increase in the grain size of the film.<sup>35,36</sup> In summary, Bi2212-*x*RE<sub>2</sub>O<sub>3</sub> (RE = Er/Y) superconducting films with high phase purity and good crystalline quality were fabricated on SrTiO<sub>3</sub>(100) substrates.

XRD- $\phi$  scans was used to analyze the in-plane orientation relationships of samples Er6 and Y6. XRD patterns were shown in Fig. 2. The  $\phi$ -scan of the Bi2212(115) and SrTiO<sub>3</sub>(110) of sample Er6 were shown in Fig. 2(a), and the  $\phi$ -scan XRD patterns of the Bi2212(115) and SrTiO<sub>3</sub>(110) of sample Y6 were shown in Fig. 2(d). As can be seen from the figures, both Er6 and Y6 exhibited good quadratic symmetry.  $\phi$  diffraction peaks on the (115) face of Er6 were 80.9°, 170.9°, 260.9° and 350.9°, which were consistent with those on the SrTiO<sub>3</sub>(110) face.  $\phi$  diffraction peaks on the (115) face of Y6 were 66.1°, 156.1°, 246.1° and 336.1°, which were consistent with the  $\phi$  diffraction peak positions of the SrTiO<sub>3</sub>(110) crystal plane. The pole figures were shown in Fig. 2(g)–(j). It can be clearly found that Bi2212 had quartic symmetry. The crystal plane (115) had four clear diffraction poles at  $\alpha = 58^\circ$ , and no other poles, indicating that the plane had only one growth orientation. The SrTiO<sub>3</sub> single crystal substrate (110) plane also had four clear diffraction poles only at  $\alpha = 45^\circ$ . This shows that the Bi2212 phase also exhibited quartic symmetry and had only one orientation. On this basis, the in-plane epitaxial matching relation of thin films was further proved by the calculation of crystal band theorem.

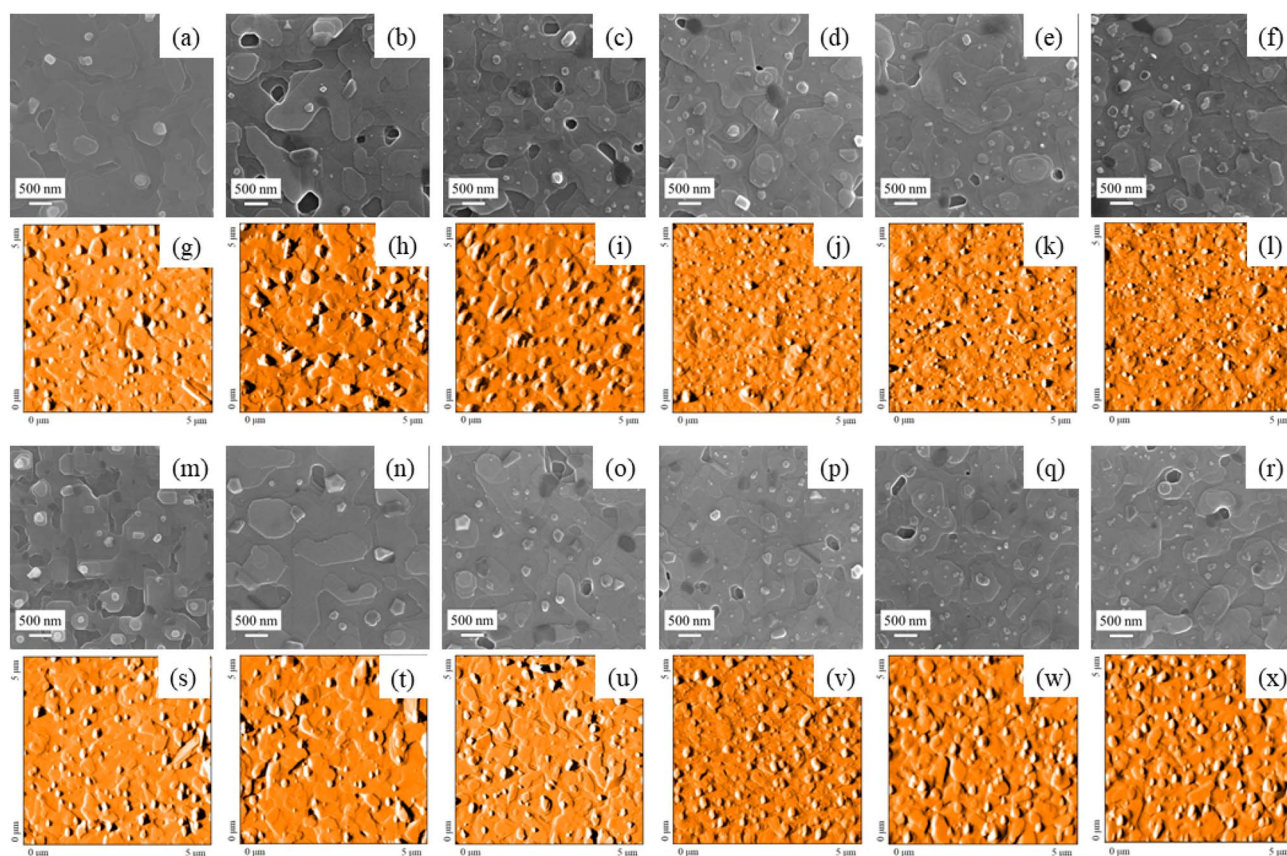


Fig. 3 SEM images and AFM images of Bi2212 superconducting films. (a)–(c) and (g)–(i) were SEM images of Er1–Er6, respectively. (d)–(f) and (j)–(l) were AFM images of Er1–Er6, respectively. (m)–(r) were SEM images of Y1–Y6, respectively. (s)–(x) were AFM images of Y1–Y6, respectively.

According to the crystal band theorem, the index  $[uvw]$  of the axial axis  $T$  of the crystal band can be expressed as (2)

$$u : v : w = \frac{h_1}{h_2} \left| \frac{k_1}{k_2} \right| \times \frac{l_1}{l_2} \times \frac{h_1}{h_2} \times \frac{k_1}{k_2} \left| \frac{l_1}{l_2} \right| = (k_1 l_2 - k_2 l_1) : (l_1 h_2 - l_2 h_1) : (h_1 k_2 - h_2 k_1) \quad (2)$$

It was calculated that  $[1\bar{1}0]$  was the crystal band axis of Bi2212(00 $l$ ) crystal plane with the (115) crystal plane. Similarly, it followed that  $[00\bar{1}]$  was the crystal band axis between the SrTiO<sub>3</sub>(100) crystal plane and the (110) crystal plane. Therefore, the in-plane matching relation between the Bi2212 substrate and the SrTiO<sub>3</sub>(100) substrate was Bi2212[100](001)  $\parallel$  STO [011](100). Meanwhile, Fig. 2(b) and (c) showed the  $\omega$ -scan XRD patterns of Bi2212(0010) and (115) for the Er6 sample, and Fig. 2(e) and (f) showed the  $\omega$ -scan XRD patterns of Bi2212(0010) and (115) for the Y6 sample, and it can be found that the in-plane and out-plane crystallinity of the Bi2212 superconducting films were good. The results showed that RE<sub>2</sub>O<sub>3</sub> doping did not change the (00 $l$ ) epitaxial growth characteristics of all the Bi2212 superconducting films on SrTiO<sub>3</sub>(100) single crystal substrates, and the films had good crystallinity.

The surface morphology of samples Er1–Er6 was characterized by FESEM and AFM, as shown in Fig. 3. Fig. 3(a)–(c) and (g)–(i) showed the SEM images of Er1–Er6, respectively. Fig. 3(d)–(f) and (j)–(l) showed the AFM images of Er1–Er6, respectively. It can be observed that the surfaces of all samples were continuous and smooth. In addition to this, the surface of the film showed mainly a lamellar structure. This was mainly due to the anisotropy of the Bi2212 growth rate. The fast in-surface growth rate resulted in a two-dimensional characteristic shape of the sample.<sup>37</sup> The surface morphology and structure of the samples Er1–Er6 was further characterized by

AFM, and as can be seen in Fig. 3(d)–(f) and (j)–(l), the lamellar morphology of the films was characterized, in agreement with the FESEM images. The surface roughness of Er1–Er6 was 12.2 nm, 11.9 nm, 17.3 nm, 11.4 nm and 11.0 nm. The roughness statistics were shown in Table 1. The doping of Er<sub>2</sub>O<sub>3</sub> did not significantly change the surface roughness. The addition of Er<sub>2</sub>O<sub>3</sub> inhibited the enrichment and growth of the precipitated phase particles, resulting in a uniform and diffuse distribution of the precipitated phase particles. The surface morphology of samples Y1–Y6 was also characterized by FESEM and AFM, as shown in Fig. 3. Fig. 3(m)–(r) showed the SEM images of Y1–Y6, and Fig. 3(s)–(x) showed the AFM images of Y1–Y6, respectively. It can be found that the surfaces of the Y1–Y6 samples continued to show a continuous and smooth lamellar morphology. The surface roughness of Y1–Y6 was 9.6 nm, 11.1 nm, 12.1 nm, 14.7 nm, 15.3 nm and 13.1 nm, respectively. The specific roughness was shown in Table 1.

The elemental distributions of the Er6 and Y6 samples were characterized by EDS spectroscopy, respectively. The results were shown in Fig. 4. Fig. 4(a) showed the surface morphology of the Er6 sample and its distribution of Bi, Ca, Cu, and Er elements, while Fig. 4(b) showed the surface morphology of the Y6 sample and its distribution of Bi, Ca, Cu, and Y elements. The distribution of Sr elements was not characterized because the SrTiO<sub>3</sub> single crystal substrate contained Sr elements. From the figure, it can be observed that the three elements Bi, Ca and Cu were uniformly distributed without component segregation in the Er6 and Y6. Similarly, no segregation was observed for Er and Y, demonstrating that Er and Y were uniformly and diffusely distributed in the film matrix.

The XPS spectra of samples Er6 and Y6 were shown in Fig. 5 to further confirm the presence of the doping elements in Bi2212 and their chemical valence. Both spectra in Fig. 5(a) and (c) confirmed the presence of bismuth, strontium, calcium, copper, oxygen and carbon in both samples, with a binding

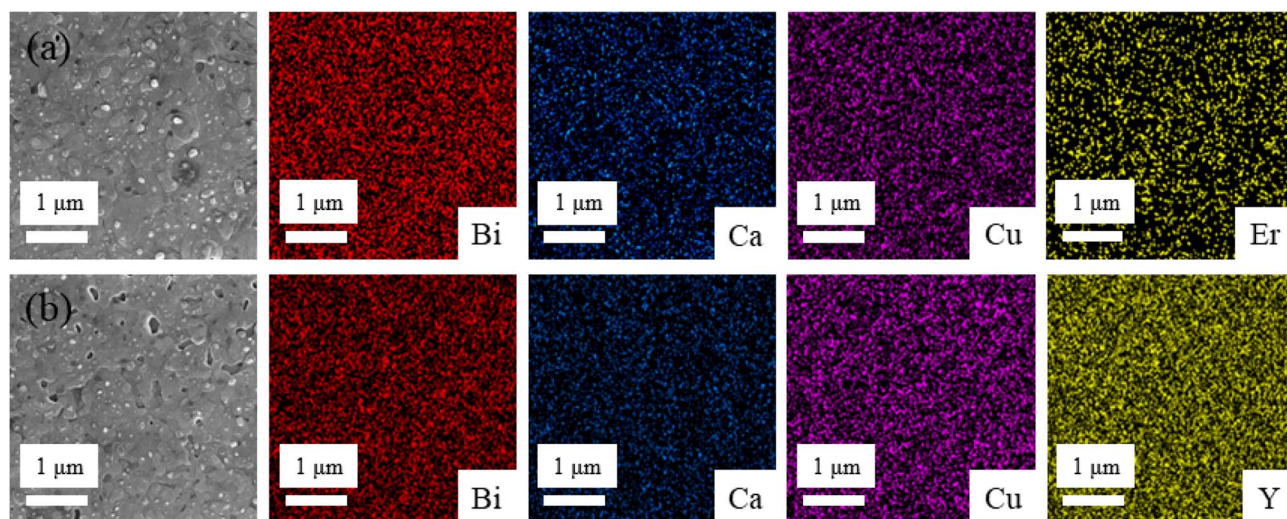


Fig. 4 Surface morphology of Bi2212 superconducting films. (a) SEM image of Er6 sample, Bi elemental distribution, Ca elemental distribution, Cu elemental distribution and Er elemental distribution. (b) SEM image of Y6 sample, Bi element distribution, Ca element distribution, Cu element distribution and Y element distribution.



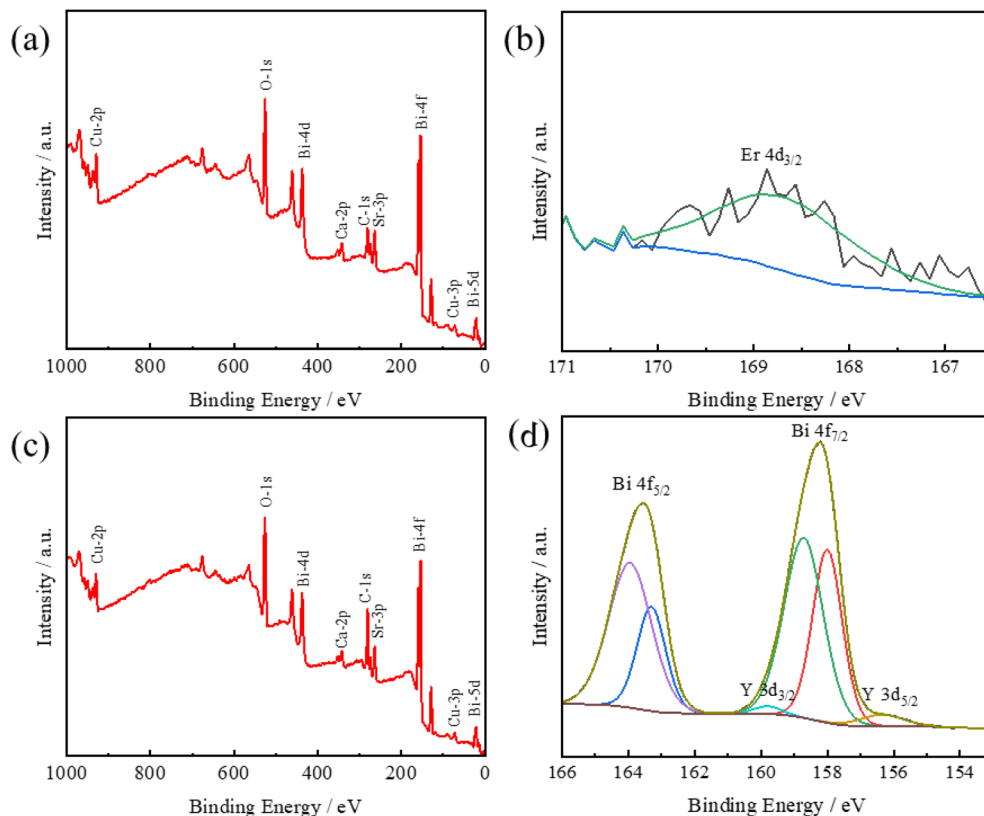


Fig. 5 XPS spectra of (a) survey scan of Er6; (b) Er region of Er6; (c) survey scan of Y6; (d) Y region of Y6.

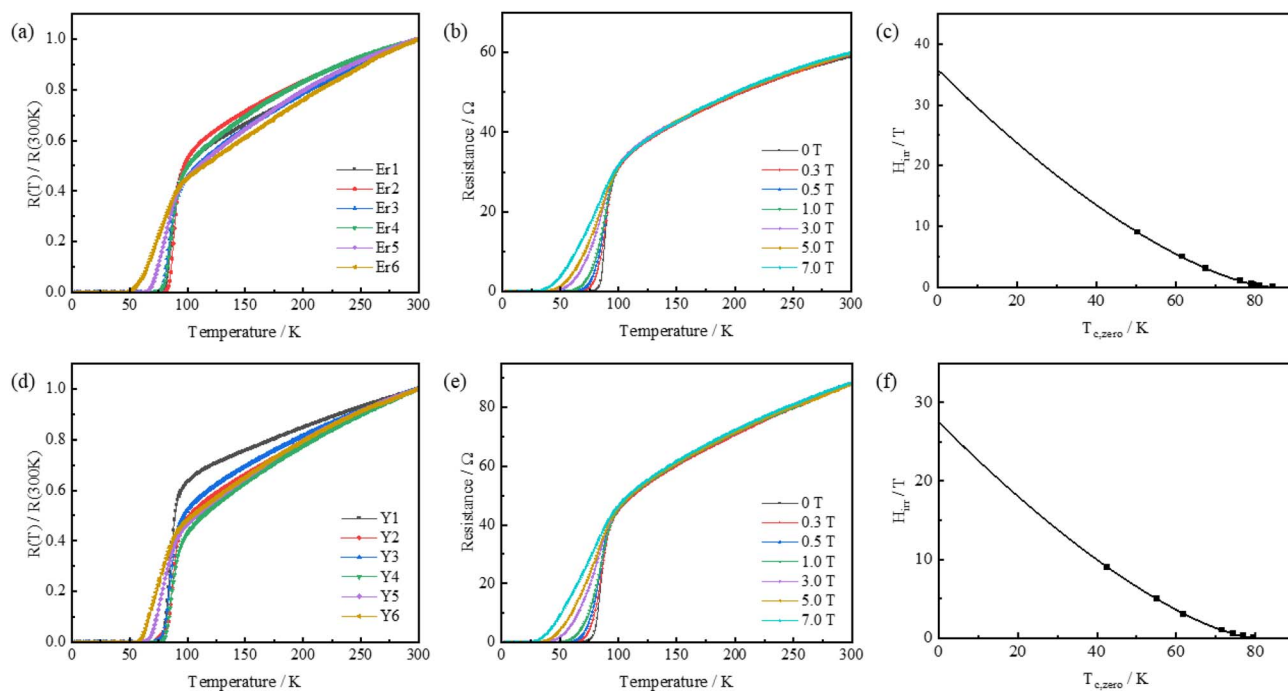


Fig. 6 (a) Electrical transport properties of samples Er group. (b) Temperature dependence of the resistances of Er2 in magnetic fields from 0 T to 9 T. (c) Temperature dependence of the irreversible field  $H_{irr}$  of sample Er2. (d) Electrical transport properties of samples Y group. (e) Temperature dependence of the resistances of Y3 in magnetic fields from 0 T to 9 T. (f) Temperature dependence of the irreversible field  $H_{irr}$  of sample Y3.

energy of 284.8 eV for C 1s, which was typical for C–C compounds and used for reference correction. The fit of Er 4d showed a peak at 168 eV as shown in Fig. 5(b), which was consistent with previously reported data.<sup>38</sup> In Fig. 5(d), the Y 3d spectrum was decomposed into two peaks at 160.5 eV and 158.3 eV, corresponding to the high bound state of Y 3d<sub>3/2</sub> and the low bound state of Y 3d<sub>5/2</sub>, respectively. These two peaks were typical of Y<sub>2</sub>O<sub>3</sub> and indicate the presence of the Y<sup>3+</sup> oxidation state in the sample.<sup>39</sup>

The electrical transport properties of the Bi2212 superconducting films were shown in Fig. 6, where Fig. 6(a) showed the electrical transport properties of the sample Er group of

Table 2 Electrical transport properties of samples

Sample	$T_{c,onset}/K$	$T_{c,zero}/K$	$\Delta T_c/K$
Er1	92.7	81.9	10.8
Er2	92.7	81.4	11.3
Er3	92.1	79.1	13.0
Er4	92.0	77.8	14.2
Er5	93.2	69.3	23.9
Er6	91.8	57.2	34.6
Y1	90.9	80.1	10.8
Y2	92.8	81.4	11.4
Y3	92.5	80.7	11.8
Y4	93.6	80.8	12.8
Y5	90.8	68.4	22.4
Y6	90.3	60.0	30.3

samples. Fig. 6(b) showed the temperature dependence of the resistance of the Er2 sample in a magnetic field from 0 T to 9 T. Fig. 6(c) showed the temperature dependence of the irreversibility field of  $H_{irr} \propto (1 - T/T_c)^{\beta_{40-42}}$  (black line) fitted to Er2, with the specific information shown in Table 2. As seen in Fig. 6(a), the sample exhibited good metallic state resistance behavior characteristics in the temperature range of 300–120 K under a magnetic field of 0 T. The temperature–resistance curve was linearly dependent. As the temperature continued to decrease, the  $R$ – $T$  curve began to deviate from the linear relationship and the resistance value decreased sharply, at which point it was the superconducting transition process. As the temperature continued to decrease, the resistance value of the film dropped to zero, at which point the sample completed. The  $T_{c,onset}$  values of Er1–Er6 were 92.7 K, 92.7 K, 92.1 K, 92.0 K, 93.2 K and 91.8 K. The  $T_{c,onset}$  values only decreased slightly at higher doping levels. This highly diffusely distributed second phase benefited from the intrinsic advantages of the sol–gel method. The atomic-level homogeneity ensured during the preparation process then greatly avoided the production of hard agglomerates of Bi2212 precursors while suppressing the agglomerative growth of the second phase material. This was a prerequisite for our preparation of Bi2212– $xRE_2O_3$  ( $RE = Er/Y$ ) with good superconductivity. The  $T_{c,zero}$  values were 81.9 K, 81.4 K, 79.1 K, 77.8 K, 69.3 K and 57.2 K. It can be seen that the  $T_{c,zero}$  values decreased monotonically with increasing doping levels. The presence of second phase material in the film. This increased the thickness of the insulating grain boundaries in the film

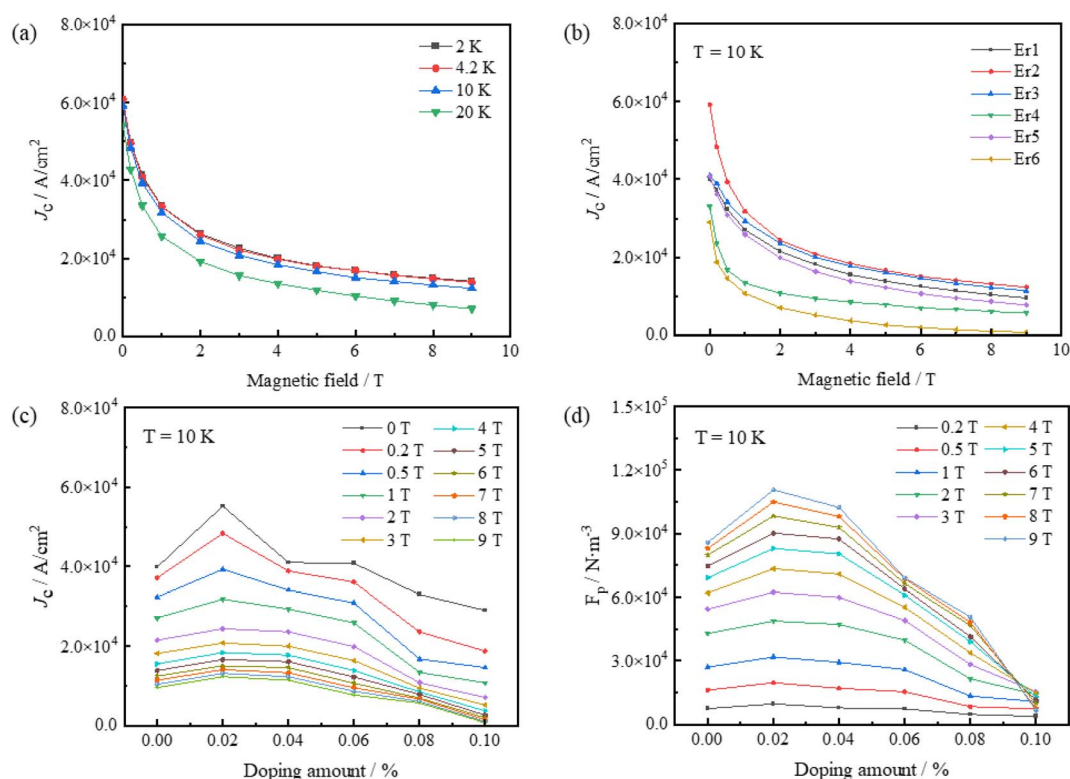


Fig. 7 (a)  $J_c$  of sample Er2 at different magnetic fields; (b) variation of  $J_c$  with magnetic field for Er group samples at 10 K; (c) variation of  $J_c$  with doping level for Er group samples at 10 K; (d)  $F_p$  versus doping level at different magnetic fields for Er group samples at 10 K.

matrix. Then, it led to an increase in the intergranular coupling energy required for the superconducting current to pass through the penetration. Thus, more grain boundary regions were required for the superconducting current to flow through to complete the superconducting transition.

Increasing the magnetic field from 0 T to 9 T, the  $R$ - $T$  curves of the Er2 sample in the magnetic field from 0 T to 9 T were shown in Fig. 6(b), the sample still showed good metallic state resistance behavior characteristics in the temperature range of 300–120 K; when the temperature continued to decrease, the  $R$ - $T$  curve started to deviate from the linear relationship, the resistance value decreased sharply and the superconducting transition process began. As the magnetic field increased,  $T_{c,zero}$  obviously moved in the direction of low temperature, and the value of  $\Delta T_c$  gradually increased. This was due to the fact that when the external magnetic field  $H_{c1} < H < H_{c2}$ , the magnetic lines of force formed a normal state core in the form of a two-dimensional pie-shaped flux vortex in the high-temperature superconductor, surrounded by a superconducting current externally. As the external magnetic field increased, resulting in an increasing normal-state core region, a decreasing superconducting fraction, a decreasing  $T_{c,zero}$  with increasing magnetic field and an increasing  $\Delta T_c$  value.<sup>43</sup> The irreversibility field ( $H_{irr}$ ) of the Er2 sample was fitted by eqn (3) and the results were shown in Fig. 6(c).

$$H_{irr} \propto (1 - T/T_c)^\beta \quad (3)$$

where  $T$  was the critical temperature value under the external magnetic field and  $T_c$  was the critical temperature value under the self-field. Where the fitted irreversible lines indicated that sample Er2 was expected to have an irreversible magnetic field of more than 30 T at 0 K. This strong irreversible magnetic field indicated that the Bi2212 superconducting film prepared by the sol-gel method had some potential applications. The  $R$ - $T$  characteristics of the group Y samples were shown in Fig. 6(d)–(f). It can be noticed that the  $R$ - $T$  properties of the group Y samples showed the same pattern, indicating that the group Y samples were Bi2212- $x$ Y $_2$ O $_3$  samples with Y $_2$ O $_3$  in the form of a second phase.

The effect of Er $_2$ O $_3$  on the critical current density ( $J_c$ ) of Bi2212 superconducting films was shown in Fig. 7. The external magnetic field was tested perpendicular to the surface of Bi2212 superconducting films ( $M \perp ab$ -plane) with a maximum magnetic field of 9 T. The variation of  $J_c$  with doping level for the samples in the Er group at 10 K was shown in Fig. 7(c). It can be seen from the figures that  $J_c$  decreased with increasing magnetic field for all samples. The decay rate decreased gradually, which was due to the joint result of the intrinsic pinning of the thin film samples and the Er $_2$ O $_3$  pinning, which was stronger at higher magnetic fields, in agreement with the above results. In addition, it can be seen that sample Er2 exhibited the highest  $J_c$  value of  $5.5 \times 10^4$  A cm $^{-2}$  compared to that of undoped sample Er1 under self-field ( $4.0 \times 10^4$  A cm $^{-2}$ ), and the current-carrying capability of Er3 ( $4.1 \times 10^4$  A cm $^{-2}$ ) was also better than that of Er1. In order to observe more intuitively the effect of Er $_2$ O $_3$

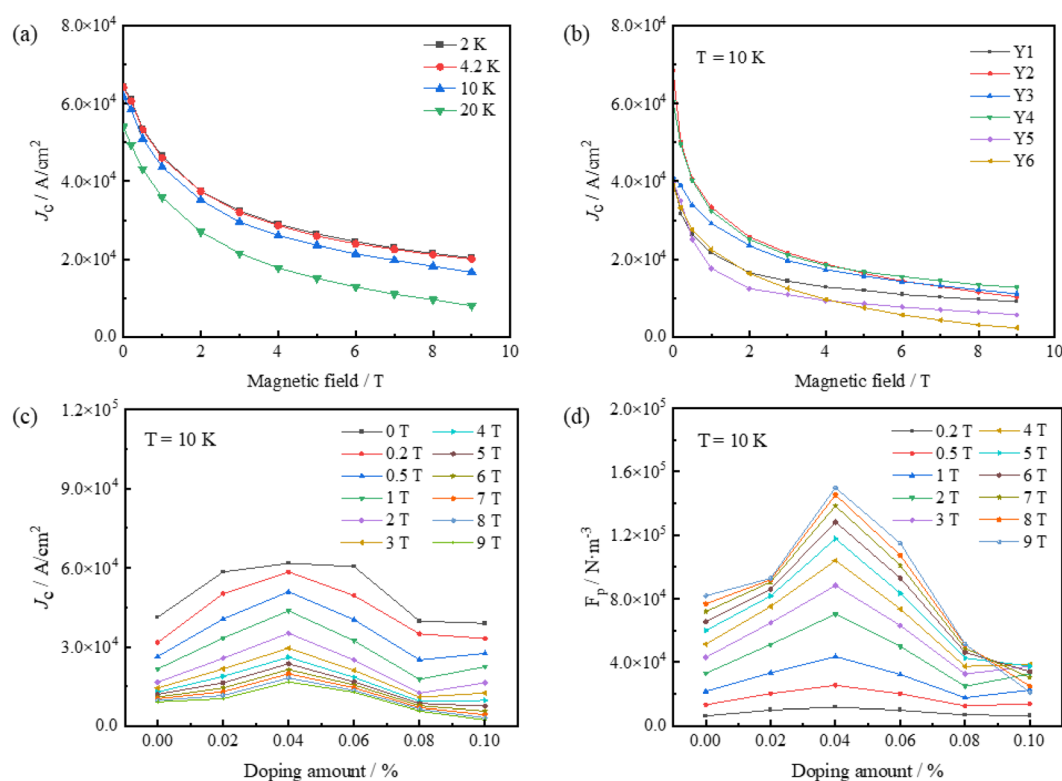


Fig. 8 (a)  $J_c$  of sample Y3 at different magnetic fields; (b) variation of  $J_c$  with magnetic field for Y group samples at 10 K; (c) variation of  $J_c$  with doping level for Y group samples at 10 K; (d)  $F_p$  versus doping level at different magnetic fields for Y group samples at 10 K.



phase doping on  $J_c$  of the Bi2212–Er-group samples, the variation of  $J_c$  with magnetic field for the Er group sample at 10 K was given in Fig. 7(b). The doping of  $\text{Er}_2\text{O}_3$  phase significantly increased  $J_c$  of the Bi2212 superconducting films and reached the maximum value at 0.04 doping level, reaching  $5.5 \times 10^4 \text{ A cm}^{-2}$  at 4.2 K self-field and  $3.2 \times 10^4 \text{ A cm}^{-2}$  at 1 T vertical external field. And Er3 also showed good current-carrying capability. However, the  $J_c$  values of the samples decreased with further doping, which was attributed to the creation of excessive second-phase defects in the samples that destroyed the superconducting region and the pinning center density exceeded the coherence length of the Bi2212 films resulting in a lower  $J_c$ . To further investigate the effect of the  $\text{Er}_2\text{O}_3$  doping density on the film properties, we calculated the macroscopic pinning force  $F_p = J_c \times M$  of the samples, which is the main means to assess the flux pinning performance of superconductors. Fig. 7(d) showed the  $F_p$  for the Bi2212 films of the Er group. Sample Er2 exhibited the largest pinning force in different magnetic fields  $F_p$ . Therefore, the best pinning effect can be obtained for Er2. At this point the doping of the second phase  $\text{Er}_2\text{O}_3$  had a more significant effect on the pinned Bi2212 superconducting film.

The effect of  $\text{Y}_2\text{O}_3$  on the  $J_c$  of Bi2212 superconducting films was shown in Fig. 8. It can be seen from the figures that the variation pattern of  $J_c$  for all samples was consistent with that of the Er group samples. Also, it can be seen that sample Y3 exhibited the highest  $J_c$  value of  $6.2 \times 10^4 \text{ A cm}^{-2}$  compared to that of undoped sample Y1 at self-field ( $4.1 \times 10^4 \text{ A cm}^{-2}$ ), and the current-carrying capacity of Y2 and Y4 ( $5.8 \times 10^4 \text{ A cm}^{-2}$  and  $6.0 \times 10^4 \text{ A cm}^{-2}$ ) was also better than that of Y1. The variation of  $J_c$  with magnetic field for group Y samples at 10 K was also given in Fig. 8(b). The doping of the  $\text{Y}_2\text{O}_3$  phase significantly increased the critical current density of the Bi2212 superconducting films and reached a maximum at a doping level of 0.08, reaching a critical current density of  $6.2 \times 10^4 \text{ A cm}^{-2}$  at 10 K for the self-field and  $4.3 \times 10^4 \text{ A cm}^{-2}$  at 1 T for the vertical external field. However, the  $J_c$  values of the samples decreased with further increase in doping. Sample Y3 exhibited the maximum pinning force  $F_p$  in different magnetic fields. Therefore, the best pinning effect for Y3 can be obtained. At this point, the doping amount of the second phase  $\text{Y}_2\text{O}_3$  had a more significant effect on the nailing of Bi2212 superconducting films. The comparison of critical current densities  $J_c$  of different

oxide doping was listed in Table 3. The comparison showed that the doping of  $\text{RE}_2\text{O}_3$  was also an effective method to improve the critical current density.

## Conclusion

In this work, (00 $l$ ) epitaxially grown Bi2212– $x\text{RE}_2\text{O}_3$  (RE = Er/Y) superconducting films were prepared by sol–gel method. The superconducting transition of the  $\text{RE}_2\text{O}_3$ -doped Bi2212 superconducting film did not change significantly with increasing doping amount, and  $\Delta T_c$  increased monotonically, indicating that the  $\text{RE}_2\text{O}_3$  phase was stacked at the grain boundaries and did not affect the lattice structure of Bi2212. The superconducting film of Er2 showed the best current-carrying capability with  $J_c$  of  $5.5 \times 10^4 \text{ A cm}^{-2}$  at 4.2 K self-field and  $3.2 \times 10^4 \text{ A cm}^{-2}$  at 1 T vertical external field. Y3 exhibited the best current-carrying capability with  $J_c$  of  $6.2 \times 10^4 \text{ A cm}^{-2}$  at 10 K for the self-field and  $4.3 \times 10^4 \text{ A cm}^{-2}$  at 1 T vertical external field. The present results provide an effective method for improving the flux pinning of Bi2212 films. And the practical application is of great importance.

## Author contributions

Bowen Zhang: conceptualization, methodology, investigation, writing – original draft. Yang Qi: conceptualization, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work is supported by National Natural Science Foundation of China (No. 61971116), China Postdoctoral Science Foundation (2021M700093), Natural Science Foundation Project of Liaoning Province (No. 2023-BS-206). Special thanks are due to the instrumental or date analysis from Analytical and Testing Center, Northeastern University.

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**Table 3** Comparison of critical current densities  $J_c$  of different oxide doping

Materials	Oxide doping	$J_c$ (A cm <sup>-2</sup> , maximum value)	Ref.
Bi2212	Er <sub>2</sub> O <sub>3</sub>	$6.1 \times 10^4$ (4.2 K)	This work
Bi2212	Er <sub>2</sub> O <sub>3</sub>	$5.9 \times 10^4$ (10 K)	This work
Bi2212	Y <sub>2</sub> O <sub>3</sub>	$6.4 \times 10^4$ (4.2 K)	This work
Bi2212	Y <sub>2</sub> O <sub>3</sub>	$6.2 \times 10^4$ (10 K)	This work
Bi2212	NiO	$5.1 \times 10^4$ (10 K)	44
Bi2212	NiO	$3.2 \times 10^4$ (40 K)	44
Bi2212	Al <sub>2</sub> O <sub>3</sub>	$1.7 \times 10^2$ (77 K)	45
Bi2212	MgO	$1.5 \times 10^4$ (77 K)	46
Bi2212	Pb <sub>2</sub> O <sub>3</sub>	$6.8 \times 10^3$ (4.2 K)	47

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