Enhanced critical current density in BaFe$_2$(As$_{0.66}$P$_{0.33}$)$_2$ nanocomposite superconducting films

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Abstract

The high upper critical field and low anisotropy of the 122-type iron-based superconductor BaFe$_2$As$_2$ makes it promising for use in superconducting high field magnets. However, its critical current density ($J_c$) in high magnetic fields needs to be further improved. Here we show that for the film prepared by pulsed laser deposition method by controlling the deposition parameters (higher substrate temperature and lower growth rate), the crystallinity of BaFe$_2$(As$_{0.66}$P$_{0.33}$)$_2$ (Ba122:P) matrix is improved while maintaining a high density of incoherent BaZrO$_3$ (BZO) nanoparticles (NPs) which together lead to significantly increased self field $J_c$. Our Ba122:P nanocomposite films also exhibit increased in-field $J_c$, reduced angular anisotropy of $J_c$, and reduced detrimental effects of thermal fluctuations (creep rate) over a wide range of temperatures and magnetic field strength. The BZO NP doped Ba122:P films show high in-field $J_c$ over 2.1 MA cm$^{-2}$ even at 4 K and 9 T ($\mu_0 H||c$), which is significantly higher than that of standard Ba122:P films and conventional alloy superconducting wires. To understand the contribution of the various pinning centers, we applied a simple model, which was developed for cuprates, to Ba122:P film with all the parameters used derived by fitting to a limited set of experimental data (no free parameters) such that temperature, angle and field properties at other experimental conditions are then calculated. This simple model fits very well to the experimental results in these two very different material systems. We discuss the effectiveness of natural defect and BZO NPs on the ratio of $J_c$ to the depairing current density. The superconducting properties for 122-type iron-based superconductors obtained through this work are considered promising for high-field applications.

Keywords: iron-based superconductors, critical current density, nanocomposite films, flux pinning

(Some figures may appear in colour only in the online journal)

1. Introduction

Ten years ago, the high critical temperature ($T_c$) Fe-based superconductor were discovered and exhibited superconductivity at 26 K, i.e. above liquid hydrogen boiling point [1]; this opens the hope for a lot of exciting applications, such as cables, generators, magnetic resonance imaging (MRI) and superconducting magnetic energy storage. In particular, 122-type Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (Ba122:Co) superconductors have been found to have attractive properties, such as a high...
critical field \( (H_{c2}) \), small mass anisotropy \([2, 3]\) and high critical current density \( (J_c) \) \([4]\). However, before reaching required performance levels, there are many scientific and technological hurdles that still need to be overcome. The Ba122 superconductors are not easily formed into flexible conductors: although the critical grain-boundary (GB) misorientation angle is more favorable than that of cuprate materials, high \( J_c \) requires near-perfect crystallinity, and superconducting performance drops rapidly in a magnetic field. The powder-in-tube technology has been progressing well for K-doped Ba122 \((\text{Ba122:K})\) \([5]\) and Ba122:Co \([6]\) wires, however, their \( J_c \) in magnetic fields is still low. On the other hand, the GB problems in Ba122 were overcome by fabrication of epitaxial thin films, which showed self-field \( J_c \) \((J_c^{s.f.})\) values in the range of over 1 MA cm\(^{-2}\) at 4 K \([4, 7–13]\). Recently, for tape/coated conductors, the Ba122 wires/films were fabricated by pulsed laser deposition (PLD) a polycrystalline substrate with intermediate oxide buffer layer produced by ion-beam-assisted deposition \([14–16]\); however, this still showed a lower in-field \( J_c \) than required for applications, thus indicating the need for improvement in flux pinning.

The decrease of \( J_c \) in a magnetic field depends on vortex motion induced by the Lorentz force and thermal activation. The ability to pin vortex flux lines is determined by the defects that have to be tailored into the material matrix without degrading the current pathway. Indeed, flux pinning has been also one of the most important topics for applications \([17–24]\) of high-temperature superconductors, such as \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) \((\text{Y123})\). Following the well-known technique of heavy ion irradiation \([25]\), amorphous tracks induced by heavy-ion irradiation of Ba122:K single crystals \([26, 27]\) were shown to enhance \( J_c \) at high fields with no \( T_c \) and \( J_c^{s.f.} \) degradation. Although heavy-ion irradiation is not practical for long-length wire and tape applications, this work shows that the Ba122 system can tolerate a very high density of defects without significant crystalline degradation. For Ba122 films, \( c \)-axis pinning due to the naturally introduced nanopillars \([28]\), or other natural defects \([10, 29]\) are enhanced in the in-field \( J_c \) close to the \( c \)-axis direction. Moreover, Ba122:Co films showed strong \( ab \)-axis pinning due to naturally introduced stacking faults, which can increase \( J_c \) around the \( ab \)-plane \([11–13]\). Although the growth rate of P-doped Ba122 (Ba122:P) can change the \( c \)-axis vertical dislocations, the naturally occurring defects are still difficult to control, indicating the need of a controllable, tunable and practical way to increase vortex pinning quasi-isotropically in Ba122 films.

Following the outstanding achievements for cuprates \([18–24]\), the addition of second phases is a potentially useful technique here also. To enhance \( J_c \), the second phase needs to be chemically stable and crystallographically compatible, and its size should be sufficiently small to avoid blocking of the current path. Based on these premises, we successfully introduced a high density of BaZrO\(_3\) nanoparticles (NPs) into Ba122:P, resulting in high in-field \( J_c \) with nearly isotropic angular dependence \([30]\). A deeper and more quantitative understanding of the effects of the complex pinning landscapes on \( J_c \) in particular and on the behavior of vortex matter in general, it is necessary to assess the potential of Ba122 films for high temperature and high field applications, and to that end it is important to explore systems with well controlled pinning landscapes.

Here, we report that a tailored ultra-high density of incoherent-interfaced BaZrO\(_3\) (BZO) NPs result in enhanced properties for \( \text{BaFe}_2(\text{As}_{0.66}\text{P}_{0.33})_2 \) \((\text{Ba122:P})\) films. The high density of BZO NPs results in virtually no degradation of the matrix crystallinity as evidenced by the further improved superconducting properties. \( J_c(H, T) \) measurements demonstrate that the NPs are highly effective as pinning centers, decreasing vortex motion and depinning fluctuation effects at both 4 and 15 K and all magnetic field strengths and orientations. Furthermore, we give a simple pinning model that predicts superconductor performance with NPs for any temperature and magnetic field using only a small set of fixed parameters.

### 2. Experimental details

Standard (undoped) \( \text{BaFe}_2(\text{As}_{0.66}\text{P}_{0.33})_2 \) and BaZrO\(_3\) (BZO) NP doped epitaxial films were deposited on MgO (100) single crystal substrates by ablating the polycrystalline PLD targets using the second harmonic \((\lambda = 532 \text{ nm})\) of a pulsed Nd:YAG laser at a repetition rate of 10 Hz in a vacuum of \( 10^{-4} \text{ Pa} \) at a substrate temperature \((T_{\text{sub}}) \) of 850°C. A 3.5 min deposition produced a film \( \sim 80 \text{ nm}\) thickness, i.e., a growth rate of 0.38 nm s\(^{-1}\). The growth rate was varied by changing the substrate-target distance. The film thickness was measured from cross-sectional TEM images at several points. We added BZO into two PLD targets at the BZO mol percent of 1% and 3%. Films were patterned using photolithography and ion milling into bridges of \( \sim 50 \mu \text{m} \) width. Additional details of the PLD target preparation have been published elsewhere \([8]\). The crystalline quality was examined by x-ray diffraction (XRD). The temperature dependence of the resistivity \((\rho)\) was measured by a four-probe method in the temperature range of 4–300 K using a Quantum Design PPMS with a superconducting magnet generating a field \( \mathbf{H} \) up to 9 T. In the PPMS, a rotational stage was used to rotate the samples with respect to \( \mathbf{H} \). The critical current was determined using a \( 1 \mu \text{V} \text{ cm}^{-1} \) criterion. Magnetization studies were performed in a Quantum Design SQUID magnetometer to characterize the creep rate \((S)\). The magnetization \((M)\) was obtained by dividing the measured magnetic moment \((m)\) by the sample volume \((V_{\text{sample}} = 80 \text{ nm thickness} \times 3.5 \text{ mm width} \times 3.5 \text{ mm length})\). For the measurements, the magnetic field was applied parallel to the \( c \)-axis of the film. The microstructure and elemental concentration mappings of the films were analyzed by transmission electron microscopy (TEM) and energy-dispersive x-ray spectroscopy, respectively.
3. Results and discussion

3.1. High density of BaZrO$_3$ NPs in BaFe$_2$As$_{0.66}$P$_{0.33}$ films

Cross-sectional elemental maps of Fe, As, Ba, P, Zr and a cross sectional TEM image for a 3 mol% BZO doped Ba122:P (Ba122:P+3BZO) film are shown in figure 1(a). From these images, the uniformly dispersed NPs, which are rich in Zr and poor in Fe, As, P, can be observed. The nano-beam diffraction pattern of the BZO NPs show that they are not coherent with the Ba122:P matrix, which is consistent with XRD patterns indicating that the BZO doped Ba122:P film shows a BaZrO$_3$(110) peak (not shown) [30]. From figure 1(b), a BZO NP can be clearly discerned within the matrix, its size being ~6 nm and ~11 nm parallel and perpendicular to the c axis, respectively (vertical arrow). Figure 1(c) shows the c and b which are the diameters along and perpendicular to the c-axis direction, respectively, in BZO NP distribution extracted from several planar (not shown) and cross-sectional STEM images. Ba122:P+3BZO film have a sharp NP distribution with an average c of 6 nm and b of 9 nm, an average NP spacing of $L_{NP} \sim 24$ nm, and density of $n_{NP} \sim 6.5 \times 10^{22}$ m$^{-3}$.

Table 1 shows a summary of the crystallographic and superconducting properties for the Ba122:P and several Ba122:P films with BZO NPs. Previously, we presented the results for a film growth at substrate temperature ($T_s$) = 800 °C and high growth rate (0.5 nm s$^{-1}$) [8, 30]. As shown in table 1, films at the previous condition show low crystallinity and low superconducting properties ($T_c$ and self-field $J_c$ ($J_c^{sf}$)). In this work, we use a new fabrication condition that deposits the film at a higher $T_s$ and lower growth rate, resulting in high crystal quality and high superconducting properties not only in standard Ba122:P but also in BZO doped films. These results are consistent with the results reported in [10] and [16] (varying $T_s$ and growth rate), showing that deposition at higher temperature and allowing more time for the atom in the Ba122:P matrix to migrate, thus increase the diffusion length for ordering. If we take a closer
Table 1. Sample data for the reference Ba122:P and for Ba122:P±BaZrO$_3$ films on single-crystal MgO. $T_{c,\text{zero}}$ was determined using an $0.01\rho_n$ criterion. $\delta\omega$ and $\delta\phi$ denote the full-width at half-maximum (FWHM) values of out-of-plane rocking curves ($\omega$ scans) of the 004 diffractions and in-plane rocking curves ($\phi$ scans) of the 103 diffractions, respectively.

| Material          | $T_{\text{sub}}$ (°C) | Growth rate (nm s$^{-1}$) | $\delta\omega$ (deg.) | $\delta\phi$ (deg.) | $T_{c,\text{zero}}$ (K) | $J_{c,f} @4$ K (MA cm$^{-2}$) | $J_{c,f} @15$ K (MA cm$^{-2}$) |
|-------------------|------------------------|---------------------------|------------------------|------------------------|--------------------------|-------------------------------|-------------------------------|
| Ba122:P           | 800                    | 0.50                      | 0.75                   | 1.03                   | 26.3                     | 3.06                          | 1.43                          |
| Ba122:P±1mol%BZO  | 800                    | 0.50                      | 0.80                   | 1.05                   | 25.3                     | 3.77                          | 2.24                          |
| Ba122:P±3mol%BZO  | 800                    | 0.50                      | 0.79                   | 1.06                   | 25.0                     | 5.3                           | 3.06                          |
| Ba122:P           | 850                    | 0.38                      | 0.63                   | 0.81                   | 26.8                     | 3.59                          | 2.02                          |
| Ba122:P±1mol%BZO  | 850                    | 0.38                      | 0.62                   | 0.79                   | 26.7                     | 5.51                          | 2.51                          |
| Ba122:P±3mol%BZO  | 850                    | 0.38                      | 0.64                   | 0.80                   | 26.6                     | 7.20                          | 3.61                          |
look at figure 1(c), the size of the BZO NP is slightly bigger \((c = 6\, \text{nm}, b = 9\, \text{nm})\) and NP density is slightly lower \((n_{np} \sim 6.5 \times 10^{22}\, \text{m}^{-3})\) at the new fabrication condition compared to that at the previous condition \((c = 5\, \text{nm}, b = 8\, \text{nm}, n_{np} \sim 7.0 \times 10^{22}\, \text{m}^{-3})\). Generally, at a higher deposition rate, more NPs remain because of the shorter diffusion length. At higher temperature, the BZO NP density decreases and size of BZO increase due to the longer diffusion length. These dependencies are very similar to those in the numerical simulation of BMO growth in PLD-Y123 film reported by Ichino et al \[31\]. Based on that simulation, the deposition parameters such as the substrate temperature, deposition rate and BMO volume fraction must be controlled to optimize the shape, size and density of BZO particles. However, these parameters must also be restricted to those that maintain good matrix crystallinity in order to achieve high superconducting performance.

The critical temperature \(T_{c,\text{zero}}\) for films with the new conditions are almost the same \(\sim 26.5\, \text{K}\) for standard Ba122:P film and the films where 3 mol% BZO was added. In particular, no decrease in \(J_{c}^{\text{f}}\) with BZO additions is found. The \(J_{c}^{\text{f}}\) of Ba122:P+3BZO films at 4 and 15 K are 7.2 and 3.6 MA cm\(^{-2}\), respectively. The \(J_{c}^{\text{f}} = 7.2\, \text{MA cm}^{-2}\) at 4 K for Ba122:P+3BZO film is almost as high as those of the Ba122:P film with a high density of c-axis correlated defects at 4 K \[10\] and irradiated K-doped Ba122 single crystal \[32\].

### 3.2. In coherent fine BZO NPs in BaFe\(_2\)As\(_{0.66}\)P\(_{0.33}\)\(_2\) films

Part of the successful addition of BZO NPs in Ba122:P can be found by the analysis shown in figure 2, by comparing structural and superconducting properties for inclusions with coherent and incoherent interfaces, i.e. coherent BaHFO\(_3\) (BHO) nanorods in GdBa\(_2\)Cu\(_3\)O\(_{6.5}\) (Gd123) films grown by using a PLD (PLD-Gd123+BHO NRs) \[33\], incoherent BZO NPs in MOD-Y123 film (MOD-Y123+BZO NPs) \[24\] and incoherent BZO NPs in PLD-Ba122:P (PLD-Ba122:P+BZO NPs). For PLD-Ba122+BZO NRs, the c-axis length of the superconducting matrix lattice expands markedly with increasing BHO NR mol\%, but in contrast remains flat for MOD-Y123+BZO NPs. Similarly, a negative trend with mol\% is observed in \(T_{c}\) and \(J_{c}^{\text{f}}\) for coherent BHO doped PLD films while for films with incoherent BMO doped MOD film, \(T_{c}\) is constant and \(J_{c}^{\text{f}}\) increases (see figures 2(b) and (c)). The c-axis expansion and \(T_{c}\) decrease in PLD-Y123+BHO NRs are consistent with oxygen deficient regions surrounding the inclusions \[34\]. For the PLD-Ba122+BZO NRs, although the c-axis slightly increases and \(T_{c}\) slightly decreases with increasing mol\% of additions, these properties still remain relatively unchanged compared to that in coherent BHO doped PLD films. As shown in figure 2(c), we found that \(J_{c}^{\text{f}}\) increases linearly with \(n_{np}\) for the cuprates and pnictides with incoherent NPs, consistent with single vortex strong pinning \[35, 36\] by NPs. For film with incoherent NPs in both Y123 and Ba122:P, a small strain is localized around the incoherent NP/matrix interfaces that leaves the matrix unaltered with just a small degradation of the superconducting properties. Therefore, some stacking faults are present and observed around BZO NPs in our Ba122:P film \[30\], similar to what are observed in some Y123 with BZO NPs \[23\]. These stacking faults also increase with increasing BZO NP density, and may also enhance pinning of BZO NPs. In progress are further investigations to understand the formation mechanism of incoherent BZO NPs in Ba122:P films.

### 3.3. High \(J_{c}\) with nearly isotropic angular dependence

We now turn to the in-field properties. In figure 3(a) we show the field dependence of \(J_{c}(H)\) at different temperatures for standard Ba122 and doped Ba122:P+3BZO films. At both 4
and 15 K, the Ba122:P+3BZO film shows significantly higher in-field $J_c(H||c)$ as compared to the standard Ba122:P film at all magnetic fields. At 4 K (see top panel in figure 3(a)), we achieved $J_c = 7.2 \text{ MA cm}^{-2}$ and $J_c = 2.1 \text{ MA cm}^{-2}$ at 9 T (corresponding to a pinning force of 189 GN m$^{-3}$) for the Ba122:P+3BZO film. At 15 K (see bottom panel of figure 3(a)), the $J_c$ values at self field and at 9 T for Ba122:P+3BZO film are $3.7 \text{ MA cm}^{-2}$ and $0.63 \text{ MA cm}^{-2}$, respectively. The values at both temperatures are higher than all previously reported Ba122-type films with natural defects [7, 10, 11] and artificial pinning centers [12, 30, 37, 38] (except the Ba122:Co film with high density of stacking faults and vertical defects [13]) and for conventional alloy superconducting wires (NbTi [39], Nb$_3$Sn [40] and MgB$_2$ [41]). As shown in figure 3(a), especially at high field, the Ba122:Co film with high density of stacking faults and vertical defects shows higher in-field $J_c$, indicating that further improvement of the performance of our films at high fields can be expected when a higher density of BZO NPs ($n_{np} > 6.5 \times 10^{22} \text{ m}^{-3}$) and a high density of natural induced correlated defects (stacking faults and vertical defects) are incorporated.

To investigate the effect of the size and density of BMO NPs on the angular dependence, we measured $J_c(H, \theta)$. The top panel in figure 3(b) shows the angular dependence of $J_c$ at 4 K and 1 T for standard Ba122:P, Ba122:P+1BZO and Ba122:P+3BZO films. The standard Ba122 film shows an anisotropic $J_c$ (the ratio $J_{c,max}/J_{c,min} = 1.64$) with no c-axis peak behavior different from that of previously reported Ba122:P film with a small c-axis peak due to c-axis correlated dislocations [10]. We observe that $J_c$ increases from that of standard Ba122:P film to that of Ba122:P+3BZO with increasing density of NPs, not only for $H||c$ but also for intermediate angles, indicating that a high density of elliptical BZO NPs effectively pin vortices over a broad angular range. The ratio $J_{c,max}/J_{c,min}$ decreases and approaches 1 with increasing density. It is worth noting that for our Ba122:P+3BZO film we achieve a $J_{c,min}$ of 5.0 MA cm$^{-2}$ at 1 T, 4 K, which is the highest value ever reported for Ba122 system films at the same field and temperature conditions. For 15 K and 3 T, we see $J_c$ of the Ba122:P+3BZO film increases for all orientations compared to standard Ba122:P and Ba122:P+1BZO, with a high $J_{c,min}$ of 1.3 MA cm$^{-2}$.

### 3.4. The relation between flux creep and NP density

The flux-creep rate $S = -\ln(J_c)/\ln(t)$ measures the rate at which vortices exit pinning centers as a result of fluctuations. These fluctuations enable vortex depinning via different types of excitations, thus effectively reducing $J_c$ [42]. In figure 4(a), we find that $S$ is significantly reduced with respect to that of standard Ba122:P when BZO NPs are added for a wide temperatures at $\mu_0H||c, 1 \text T$. As shown in the inset of figure 4(a), for BZO($D_{np} \sim 9 \text{ nm}$, $D_{np}/2\xi_{ab}(T)$—varies

![Figure 3](image-url)
between —1.6 and <1 at low \( T \leq 15 \text{ K} \) and high temperatures, respectively. Based on the results in strongly NP doped Y123 films, values of \( D_{\text{NP}}/2\xi_{ab}(T) > 3 \) or <1 lead to less effective pinning \([24, 30]\); thus the ability of the 9 nm BZO NPs to increase \( J_c \) is higher and is retained over a wide temperature ranges. Recently, the optimum size of NPs for enhancing the in-field \( J_c \) was simulated using the time-dependent Ginzburg–Landau model, which suggests that the optimum size of NPs depends on the magnetic field \([43]\) as well as on temperature.

The stronger the pinning the smaller the \( S \), but more importantly, the reduction of \( S(H) \) continues up to higher fields with increasing density of BZO NPs; the maximum field for the low creep onset \( (\mu_0H(S_{\text{onset}})) \) is 3 T (the inter-vortex distance \( a_f = 28 \text{ nm} \)) for the Ba122:3P film with and without BZO NPs, NbTi \([44]\), MgB\(_2\) \([44]\), and YBCO with and without BZO NPs. Vertical arrows indicated that addition of incoherent BZO NPs have reduced \( S \) towards the limit.

**Figure 4.** (a) Temperature dependence of \( S \) for the Ba122:P and Ba122:P+3BZO films at \( H \lvert\lvert c \) and 1 T. Inset of (a) indicate temperature dependence of the size ratio \( (D_{\text{NP}}/2\xi_{ab}(T)) \) for Ba122:P+3BZO film. (b) Field dependence of the flux creep rate \( S \) for the Ba122:P and Ba122:P+3BZO films at \( H \lvert\lvert c \) and 4 K. (c) \( S \) at \( T = T_c/4 \) and \( \mu_0H = 1 \text{ T} \) versus \( G_i^{1/2} \) for Ba122:P film with and without BZO NPs, NbTi \([44]\), MgB\(_2\) \([44]\), and YBCO with and without BZO NPs. Vertical arrows indicated that addition of incoherent BZO NPs have reduced \( S \) towards the limit.
The magnitude of the creep rate is correlated with the Ginzburg number \( G_i \), which captures the strength of thermal fluctuations in a superconductor and depends on material-specific parameters. The \( G_i \) can be estimated \( G_i \approx \gamma^2 T_c^2 \lambda^4 / \xi^2 \) where \( \gamma \) is the electronic mass anisotropy, \( \lambda \) is the penetration depth the and \( \xi \) is the coherent length. Because the \( G_i \sim 10^{-2} \) in \( Y123 \) is orders of magnitude larger than \( G_i \sim 10^{-8} \) in \( NbTi \), it is universally accepted that this difference roughly accounts for the much faster creep in \( Y123 \). We obtained intermediate \( G_i \sim 1.2 \times 10^{-4} \), calculated using \( \gamma = 1.5 \) [8], \( \lambda_{ab}(0) = 230 \text{ nm} \) and \( \xi_{ab}(0) = 2.5 \text{ nm} \) [45] for \( Ba122:Plms \). Eley et al did find a universal lower bound for low creep rates which depends on \( Gi^{0.5} \) and \( T/T_c \) [44]. Figure 4(c) shows the creep rate at \( T = T_c/4 \), \( \mu_0 H = 1 \text{ T} \) for a few materials including our \( Ba122:Plms \) with and without BZO NPs, \( NbTi \) [44], \( MgB_2 \) [44], and \( Y123 \) films with and without BZO NPs. More detail and additional data for many materials can be found in [43]. The straight line at \( S \sim Gi^{0.5} / 4 \) demarcates a region of unobtainable \( S \) values; strikingly, no data appear below it. From figure 4(c), we are able to reduce the creep rate by the introduction of effective pinning centers (see vertical arrows for \( Ba122:Plms \) and \( Y123 \)) and reduction of the Ginzburg number. It is worth noting that for our \( Ba122:Plms+3BZO \) film we achieve a \( S \) of 0.0068 at 1 T and \( T/T_c = 0.25 \), which is the lowest value ever reported among all iron-based superconductor in same field and temperature conditions. Moreover, the value achieved for the \( Ba122:Plms+3BZO \) film is as small as the \( S \) for \( NbTi \) and \( MgB_2 \), which are already used in solenoid magnets in MRI systems and do operate in ‘persistent mode’.

3.5. Simple pinning model for superconductor with strong pinning NPs

We have seen the clear effect of a high density of BZO NPs on the enhancement of \( J_c \) and reduction of thermal activation for \( Ba122:Plms \) films. The challenge is to quantify improvements so as to be able to target specific applications based on \( J_c(T, H, \theta) \). Several models have been proposed to explain \( J_c(T, H, \theta) \) in cuprate and pnictide superconductors with strong pinning centers [23, 46–56]. Although the influence of creep on \( J_c \) for these superconductors has been known for a long time [41, 57], only a few attempts have been made to link the pinning improvements to \( J_c \) and \( S \) [57, 58]. Recently, we developed a simple pinning model [24] to statistically account for the contributions from different pinning centers with the novelty that it takes into account the effect of vortex creep to determine the correct statistical contribution to \( J_c \).

To calculate the temperature, magnetic field and field angle dependence of \( J_c \) \( (J_{c,cal}) \) for pnictide superconductors films, we use \( J_{c,cal}(T, H, \theta) = J_{c0}(T, H, \theta)(1 - S \ln (t/t_0)) \) where \( t_0 \) is the effective attempt time, \( J_{c0} \) is the creep-free \( J_c \) and \( S \) is the experimentally obtained flux-creep rate. Based on the data from figure 1(c), in figure 5 we model the NPs as elliptical. Since the BZO NPs are strong pinning centers \( (D_{np} \gg 2\xi_{ab}) \), we can assume a linear summation for the volume

![Figure 5. (a) Cross-section and (b) plan-view sketch of vortex core pinned by strong nanoparticles \( (D_{np} \gg 2\xi_{ab}) \). We used \( c/b = 0.7 \).](image_url)

Table 2. Values used in the calculation of \( J_c \) for \( Ba122:Plms+1BZO \) and \( Ba122:Plms+3BZO \) films shown in figure 6. \( B_c(0) = 0.38 \text{ T} \) is calculated by \( B_c(0) = \mu_0/(2\sqrt{2} \pi \lambda_{ab}(0) \xi_{ab}(0)) \) using \( \lambda_{ab}(0) = 230 \text{ nm} \) and \( \xi_{ab}(0) = 2.7 \text{ nm} \).

| Material          | \( T_{c,zen} \) (K) | \( \gamma @ T \) | \( \gamma @ 15 \text{ K} \) | \( B_c(0) \) (T) | \( c/b \) | \( n_{np} \) \( (\times 10^{21} \text{ m}^{-3}) \) | \( t/t_0 \) | \( B_c(2) \) (T) | \( l_d(\text{nm}) \) |
|-------------------|---------------------|-----------------|-----------------|----------------|--------|-------------------------|--------|----------------|----------------|
| \( Ba122:Plms+1BZO \) | 26.7                | 1.3             | 1.5             | 0.38           | 6/9    | 0.7                     | 40     | 20              | 50              | 6               |
| \( Ba122:Plms+3BZO \) | 26.5                | 1.3             | 1.5             | 0.38           | 6/9    | 0.7                     | 65     | 20              | 50              | 6               |
pinning force density in the creep-free case:

\[ F_{\text{NPs}} = J_{c0}^N \mu_0 H = n_{np} f_0 = n_{np} \frac{dU_p}{dx} \]

\[ = n_{np} \frac{V_{np}(\mu_0 H_c(T))^2/2 \mu_0)}{2 \xi_{ab}} \]

\[ = n_{np} \left[ 1(\theta) \left( \frac{\mu_0 H_c(T)^2 \pi \xi_{ab}(T) \varepsilon(\theta)}{4 \mu_0} \right) \right] \]

\[ = n_{np} \left[ \frac{\mu_0 H_c(T)^2 \pi \xi_{ab}(T)}{4 \mu_0} \right] \left( \frac{\cos^2 \theta + \gamma^{-2} \sin^2 \theta}{\cos^2 \theta + (c/b)^2 \sin^2 \theta} \right)^{0.5} , \tag{1} \]

where \( \mu_0 H_c \) is thermodynamic critical field, \( n_{np} \) is the BZO NP density and \( l(\theta) = l_0(\cos^2 \theta + (c/b)^2 \sin^2 \theta)^{-0.5} \) is the mean size of the NPs, which includes the ellipticity as \((c/b)\). The NP diameter along and perpendicular to the c-axis direction are \( c \) and \( b \), respectively. \( V_{np} \) is the volume of NP and \( \varepsilon(\theta) = |\cos^2 \theta + \gamma^{-2} \sin^2 \theta|^{0.5} \). From the temperature and field dependence of \( J_{c0} \) proposed by Matsumiita \[57\] and equation (1), the creep-free \( J_c \), \( J_{c0}(T, H, \theta) \), for BMO NPs is expressed as

\[ J_{c0}^{NP}(T, \theta, H) = \frac{n_{np}}{\mu_0 H} \left( \frac{\gamma(\mu_0 H_c(0))^2 \pi \xi_{ab}(0) l_0}{4 \mu_0} \right) \left( \frac{\cos^2 \theta + \gamma^{-2} \sin^2 \theta}{\cos^2 \theta + (c/b)^2 \sin^2 \theta} \right)^{0.5} \]

\[ \times \left( \frac{1}{T \xi_{ab}(T)} \right) \left( \frac{l_0}{\mu_0 H_c(T)} \right)^{0.5} \left( \frac{1}{\mu_0 H} \right)^{2} , \tag{2} \]

where the temperature dependence is simply assumed as \( H_c(T) = H_c(0)(1 - T/T_c) \) and \( \xi_{ab}(T) = \xi_{ab}(0)(1 - T/T_c)^{-0.5} \); the field dependent factor \( (1 - H/H_c(T))^2 \) comes from the reduction in the condensation energy \[59\]. We focus on the additional pinning from NPs, assuming that the rest of the pinning landscape remains unchanged. In order to take into account the effect of fluctuations, \( J_{c0} \) needs to be
calculated, to which is then added the NP contribution using statistical summation [60, 61]. Using \( J_{c0}^{\text{stan.}}(T, H, \theta) = J_{c0}^{\text{exp.}}(T, H, \theta) / (1 - S_{\text{stan.}} \ln (t/t_0)) \), where \( J_{c0}^{\text{exp.}}(T, H, \theta) \) is the experimental \( J_c \) for standard Ba122:P film, the calculated \( J_c \) for a BZO doped sample would be

\[
J_{c,\text{cal.}}^{\text{BZO}}(T, H, \theta) = [J_{c0}^{\text{stan.}}(T, H, \theta)^2 + J_{c0}^{\text{NP}}(T, H, \theta)^2]^{0.5} \times (1 - S_{\text{BZO}} \ln (t/t_0))
\]

The parameters used are listed in table 2.

Figure 6(a) shows the temperature dependence of the experimental \( J_c \) (symbols) and calculated \( J_c \) (solid lines) for the Ba122:P+1BZO and Ba122:P+3BZO films at \( H \parallel c = 1 \, \text{T} \). Using as average NP size \( d_{\text{BZO}} \) from microstructural data and the experimentally measured \( S(T) \), in figure 6(a) we show that the calculated \( J_c \) values for both films are in good agreement with the experimental \( J_c \). The field dependence of the calculated \( J_c \) at \( H \parallel c \) and 4 K for both Ba122:P+1BZO and Ba122:P+3BZO films is again in very good agreement with the experimental \( J_c(T) \) data shown in figure 6(b). Figures 6(c) and (d) show the angular dependences of the measured \( J_c \) (symbols) and the calculated \( J_c \) (lines) for the BZO NP doped films at (4 K, 1 T) and (15 K, 3 T). The agreement is very satisfactory in both cases given that the temperature difference induces big changes in the superconducting values that are taken into account by the model using the same parameter values. The most important feature of the present model is that all the parameters used are derived by fitting to a limited set of experimental data (no free parameters) and that temperature, angle and field properties at other experimental conditions are then calculated. We show the effectiveness of our simple pinning model in the case of adding NPs for not only cuprate [24] but also pnictide films.

3.6. The ratio between \( J_c \) and depairing current \( (J_d) \)

The depairing current \( (J_d) \) can be estimated by \( J_d = \frac{\phi_0}{4.22 \pi \lambda_0 \xi_0} \), where \( \phi_0 \) is the flux quantum and the temperature dependence is simply assumed as \( \lambda_{ab}(T) = \lambda_{ab}(0)(1 - T/T_c)^{-0.5} \). For calculation of \( J_d \) in Ba122:P, we use \( T_c = 31 \, \text{K} \), \( \lambda_{ab}(0) = 230 \, \text{nm} \), \( \xi_{ab}(0) = 2.7 \, \text{nm} \) [42] resulting in \( J_d = 73 \, \text{MA cm}^{-2} \) at 0 K. The top and bottom panels in figure 7(a) show the temperature dependence of \( J_c^{\text{St}} \) and the ratio of \( J_c^{\text{St}}/J_d \) for Ba122:P films with and without BZO NPs. As shown in the top of figure 7(a), \( J_c^{\text{St}}/J_d \) for +3BZO films shows about 2.4 times higher \( J_c^{\text{St}} \) compared to that of standard Ba122:P films at all temperatures, indicating a clear effect of the BZO NPs on the enhancement \( J_c \). The calculated \( J_d \)

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**Figure 7.** Temperature dependence of \( J_c^{\text{St}} \) and \( J_c^{\text{St}}/J_d \) for (a) Ba122:P and Ba122:P+3BZO (2.5 vol% BZO) films and (b) Y123 and Y123+5BZO (2.5 vol% BZO) films.
indicates that we have achieved \( \approx 14\% \) of \( I_d \) by introducing the high density \( (n_{\text{np}} \approx 6.5 \times 10^{22} \text{m}^{-3}) \) and of similar size to a vortex core \( (D_{\text{NP}} \approx 2\ell_{\text{a}c}) \). The ratio, \( \frac{I_c^s}{I_d} \), is as high as in irradiated Ba122:K \cite{62} single crystals.

Comparison of the \( I_c^s \) and \( \frac{I_c^s}{I_d} \) ratio for pnictide and cuprates films, the \( J_{c,s}^f \) and \( \frac{J_{c,s}^f}{J_d} \) for standard Y123 and 5 mol% of BZO doped Y123 \((Y123+5\text{BZO NPs})\) films grown by MOD are shown in figure 7(b). The thickness of both Y123 films with and without BZO NPs is \( \approx 600 \) nm. As shown in the top panel of figure 7(b), \( J_{c,s}^f \) for Y123 + 5BZO film shows twice the \( J_{c,s}^f \) than that of standard Y123 films for all temperatures, indicating a clear effect of a BZO NPs on the enhancement of \( J_c \). We start with comparing the standard Y123 and standard Ba122 films. Although the \( I_c^s/I_d \) for standard Ba122-P is only \( \approx 6\% \), the \( I_c^s/I_d \) is \( \approx 8\% \) for standard Y123 films. We consider that this difference attributed to misorientation angles at grain boundaries and pinning by natural dislocations induced naturally during growth condition. For misorientation angles at grain boundaries, \( \theta \), \( \phi \approx 0.8 \) deg. for Ba122-P film is only half of \( \phi \approx (2.2 \) deg.) for the Y123 films because the latter films were deposited on oxidized buffered metallic substrates (i.e., coated conductors) rather than single crystal substrates. Moreover, several papers \cite{4,63} reported that the \( \phi \) dependence of \( I_c^s \) for Ba122 film is less sensitive than that for Y123 films. This would imply that the \( I_c^s/I_d \) should be smaller for standard Y123 films \( (\phi \approx 2.2 \) deg.) compared to Y123 film indicating that another factor must be responsible for the larger \( I_c^s/I_d \). MOD Y123 film is known to have a high density of negative defects i.e. twin boundaries acting as \( c \)-axis correlated pinning centers and stacking faults parallel to the \( ab \) plane \cite{64}. Therefore, the smaller \( J_{c,s}^f/I_d \) in Ba122-P film is probably related to its lower density of natural defects.

By adding BZO NPs to Ba122 films, we are able to achieve \( J_{c,s}^f/I_d \) values as high as 15%, which is as high as has been achieved in BZO NP doped Y123, and 2.5 times higher than for standard B122 as shown in figure 7(b). Recently, Sato et al. reported that vertical dislocations in Ba122:Co films could be controlled by changing the growth rate, resulting in high \( J_{c,s}^f \) and in-field \( J_c \) without addition of any other artificial pinning centers \cite{10}. As we reported \cite{64} for BZO NPs doped Y123 films that such \( c \)-axis correlated natural defect act as important pinning centers in addition to the high density of BZO NPs not only below the matching fields but also at high fields. For further enhancement of \( J_c \) for our Ba122 films, how to tailor the size and density of both naturally present defects and strong-pinning artificial NPs without degradation of the crystallinity and superconducting properties of the matrix is key. Hence, a combination of tailored pinning centers of different dimensions (dislocations \((1D)\), plane stacking faults \((2D)\) or incoherent-BaZrO3 NPs \((3D)\)) while ensuring that the underlying matrix remains as pristine as possible will yield better performing Ba122-P films and coated conductors.

4. Conclusion

In summary, we have demonstrated the ability of adding a large number of non-superconducting phase NPs of tunable density without affecting the host matrix. At high density \((6.5 \times 10^{22} \text{m}^{-3})\) and small size \( (9 \pm 5 \) nm) BaZrO3 NPs increase \( J_c \), reduce the anisotropy of angular dependence of \( J_c \) (the ratio \( J_{c,max}/J_{c,min} \approx 1.3 \)) and reduce detrimental effects of thermal fluctuations (creep) over a wide range of magnetic field strengths and temperatures. The BZO NP doped Ba122: P films exhibit a high \( J_{c,s}^f \) of 7.2 MA cm\(^{-2}\) and high in-field \( J_c \) over 2.1 MA cm\(^{-2}\) even at 9 T, \( (\mu_0 \text{H})/c \) which is over 8 times higher than that of a standard Ba122:P film. Even at 15 K and 3 T, we achieved a \( J_c \) over 1.3 MA cm\(^{-2}\), which is three times higher than the \( J_c \) observed in MgB\(_2\) \((15 \) K, 3 T) and NbTi \((4 \) K, 3 T). Further improvement of the performance of our films can be expected when correlated defects are incorporated. BZO NP doped Ba122:P film has a very low creep rate, as small as that of MgB\(_2\) and NbTi, a higher \( J_c \) and the a small anisotropy. BZO NP doped Ba122:P film has a very low creep rate, as small as that of MgB\(_2\) and NbTi, a higher \( J_c \) and the a small anisotropy. If these properties can be maintained on a metallic substrate, BZO NP doped Ba122:P could be used to make high field magnets, such as MRIs operating in the ‘persistent mode’ for operation in the temperature range up to 15 K.

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