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FLUX PINNING AND PROPERTIES OF SOLID-SOLUTION $(Y,Nd)_{1+X}Ba_{2-x}Cu_3O7_{-\delta}$ SUPERCONDUCTORS PROCESSED IN AIR AND PARTIAL OXYGEN ATMOSPHERES (PREPRINT)

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14. ABSTRACT

The effect of chemical composition substitutions on the flux pinning and physical properties of $(Y,Nd)\ 1 + XB_{a2}\text{-}xCu_3O7_{-\delta})$ superconductors was studied in powders processed by solid-state reaction and equilibrated in air at 910 °C. The powders were subsequently processed in 1% O2 atmosphere at <920 °C to increased the superconducting transition temperature (Tc) and critical current density (Jc). After processing in air, the powders were nearly pure single-phase compositions as determined by X-ray diffraction. Powders were finally annealed in 100% O2 atmosphere at temperatures <500 °C to maximize Tc. the Tcs of the powders were measured by ac susceptibility and dc magnetization methods. Annealing powders with a final step in 1% O2 atmosphere compared to processing in air significantly enhanced Tc from 65-90 K to >92 K for all compositions tested, and also increased Jc from about ~ 10^3 - 1 0^5 A/cm^2 to ~10^6 A/cm^2. The flux pinning properties varied depending on exact composition, and the intrinsic behaviors changed with the final 1% O2 annealing treatment.

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FLUX PINNING and PROPERTIES OF SOLID-SOLUTION $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ SUPERCONDUCTORS PROCESSED IN AIR and PARTIAL OXYGEN ATMOSPHERES

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ABSTRACT

The effect of chemical composition substitutions on the flux pinning and physical properties of $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconductors was studied in powders processed by solid-state reaction and equilibrated in air at 910°C. The powders were subsequently processed in 1% O_2 atmosphere at < 920°C to increase the superconducting transition temperature (T_c) and critical current density (J_c). After processing in air, the powders were nearly pure single-phase compositions as determined by X-ray diffraction. Powders were finally annealed in 100% O_2 atmosphere at temperatures < 500 °C to maximize T_c. The T_cs of the powders were measured by ac susceptibility and dc magnetization methods. Annealing powders with a final step in 1% O_2 atmosphere compared to processing in air significantly enhanced T_c from 65-90 K to > 92 K for all compositions tested, and also increased J_c from about ~10^3-10^5 A/cm^2 to ~10^6 A/cm^2. The flux pinning properties varied depending on exact composition, and the intrinsic behaviors changed with the final 1% O_2 annealing treatment.

INTRODUCTION

High transition temperature (Rare-Earth)$Ba_2Cu_3O_{7-z}$ (RE123) superconductors are being considered for applications including thin film coated conductors and bulk devices because of their high superconducting transition temperatures (T_c) > 90 K, and enhanced critical current density (J_c) at 77 K in useful magnetic fields. While these materials have desirable qualities at 77 K, it is of interest to increase

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the $J_c(H)$ properties even further by increasing the flux pinning properties of the superconductor. Different methods can be considered to introduce flux pinning defects into the superconductors, including irradiation and addition of second-phase defects or precipitates. One method being considered for bulk applications is to substitute rare-earth cations into the RE123 compound. Different variations of this theme have been studied, including substitution in (Y,R)123 with R = Ho, Dy, Gd, Eu, and Pr, and various other combinations of rare-earths such as (Gd,Sm,Eu)123 [1-16]. Possible mechanisms by which such substitutions increase the flux pinning include: **(a)** addition of second-phase defects by precipitation or composition changes, **(b)** formation of finely distributed lower T_c components from the mixed solubility of RE with Ba and intersolubility of RE or other mechanisms, or **(c)** randomly distributed oxygen-deficient zones which have lower T_cs [7,8]. The finely distributed lower T_c components are suggested as a cause of the so-called 'fishtail' effect, where as the magnetic field is increased, the J_c increases as the lower T_c components transition to normal behavior before the J_c decreases at much higher applied magnetic fields [7,8]. The peak of J_c maximum in these materials typically occurs at applied fields of about 2 T to 3 T.

Studies of the system $(Y_{1-x}Nd_x)Ba_2Cu_3O_{7-\delta}$ have, to our knowledge, been limited thus far to melt-processed or single crystal materials [9-14], and powders [15,16]. Single crystals in this system demonstrated very high J_c and the 'fish-tail' effect for Nd content varying from 0.1 to 0.4 after varying oxygenation treatments [13]. Recently our group published initial studies on $(Y_{1-x}Nd_x)Ba_2Cu_3O_{7-\delta}$ powders processed in air [16].

In this paper, previous studies on powders in this system [16] are continued by adding an additional processing step of annealing in reduced oxygen atmospheres to enhance T_c and J_c. The T_c in particular was noted to be quite low for some of the Nd-rich and Ba-poor compositions after annealing in air [16]. Subsequent processing in reduced oxygen atmospheres is well known to sharpen the T_c transition of Nd123 type compositions and improve superconducting properties [15]. How effective this is for processing the mixed compositions and their effect on flux pinning is studied herein.

In this and previous work, the effect of composition changes in $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ was studied in solid-state powders annealed in air to achieve chemical equilibrium [16]. Powder compositions are expected to have different properties than (Y,Nd)123 melt-processed or crystals in previous studies, where non-equilibrium processes can affect the physical properties. In melt-processed materials it is almost impossible to eliminate the formation of second-phase defects such as RE211, which can affect pinning. With powder processing, it is possible to completely eliminate second-phase defects, and investigate other causes of pinning more related to the intrinsic properties of the crystal structure.

For the studies herein, powders were annealed in 1% oxygen atmosphere, which is expected to enhance site occupation of Nd on the RE rather than Ba site [15,17]. This is expected to sharpen and increase the T_c transition, however it could decrease flux pinning by reducing the formation of lower T_c solid-solutions [8,15,16].

In this paper, only solid-solution single-phase compositions are considered that preserve the single-crystal structure however perturb the superconductor in localized regions surrounding the chemically substituted volumes. It's expected that with Nd substitution on about 5 % or 10% of the Y or Ba sites, the defect density of the locally-perturbed areas can be high enough for effective pinning ~ 2-3 x10^{11} cm^{-2} equivalent to a fluxon density of about 3-6 T. How effectively this can increase the flux pinning must be determined, however.

EXPERIMENTAL**

Experimental methods for this work are described in the following, using procedures identical to previous work [16]. Superconducting powders were prepared by the solid-state reaction method, using starting reactants of Nd_2O_3, Y_2O_3, $BaCO_3$, and CuO (≥ 99.95% purity). The powders were dehydrated at 450 °C prior to weighing. The powders were mixed and ground with mortar and pestle, calcined by slow heating 650 °C to 850 °C at 25 °C/h, and subsequently annealed with intermediate grinding at 880 °C and 910 °C. Powders were annealed at 910 °C with intermediate grinding until phase equilibrium was reached (3-4 annealings), as determined by X-ray diffraction (XRD). The powders were reacted in ~1 cm diameter pellets (0.5 g to 1 g batches), formed by lightly pressing (5-10x10^6 Pa) in molds. X-ray diffraction was performed with a Rigaku diffractometer. A step size of 0.03° was used for the θ-2θ scans.

After single-phase compositions were obtained, an additional processing step in 1% O_2 atmosphere was performed; the annealing temperature was at 820°C to 920°C increasing in 20°C increments as the Nd content increased from 0 to 1.0, and pellets were reacted on mixed (Nd,Y)211 pellets to minimize reactions with the substrate. After annealing in 1% O_2 atmosphere, the samples were checked with XRD to determine if the single phase composition was preserved or whether some slight (melting or decomposition) reaction might have occurred to cause formation of Y_2BaCuO_5 and $BaCuO_2$ phases (for example). A final annealing step was performed in 100% O_2 atmosphere at 460°C to 260°C, decreasing in 40°C increments as the Nd content increased from 0 to 1.0; this assumed a linear gradient in temperature between optimized annealing temperatures for Y123 and Nd123 compositions [18]. The optimal annealing temperature in 100% O_2 atmosphere for the mixed RE123 compounds to maximize oxygen content and T_c is unknown yet, therefore this approximation was used.

Superconducting properties of powders were measured with a SQUID magnetometer (Quantum Design, MPMS/$MPMS^2$). Magnetization-applied field (M-H) hysteresis loops at different temperatures were made by heating samples to 100 K and zero-field cooling (ZFC) to the measurement temperature. The magnetic J_c was estimated using the extended Bean critical current model $J_c = 15(\Delta M)/R$ where ΔM is the volume magnetization, and R is the radius of the superconducting volume roughly approximated as 0.00005 cm for the finely reacted and ground powders [19].

Field-cooled (FC) Meissner and zero-field-cooled (ZFC) measurements were performed from 5 K to 100 K [19]. The SQUID magnet was reset to zero before any measurements. The superconducting volume percentages were calculated using $\chi(\%) = 4\pi\chi_v/(1-D*4\pi\chi_v)$, where $\chi_v = M/H_{appl}$ is the measured magnetic susceptibility, and D = 1/3 is the demagnetization factor assuming a spherical particle distribution [19]. The applied magnetic field was H_{appl} = 796 A/m - H_{rem}, where H_{rem} is the remnant field of the magnet after resetting to zero, determined for each sample by measuring M(H) from 796 A/m to -398 A/m at 79.6 A/m intervals and plotting when M = 0 (± 8 A/m accuracy). The transition temperature of the largest volume fraction of powder was determined by finding the temperature when $(d^2\chi/dT^2) \cong 0$ upon cooling from 100 K. The standard uncertainty of T_c measurements was 0.5 K, as determined from both ZFC and FC curves and multiple measurements. The standard uncertainty of Meissner volume fractions was ± 5%, as determined from multiple measurements of one sample. The standard uncertainty of J_cs was measured using differences of ΔM for both positive and negative applied fields. Standard uncertainties for normalized $J_c(H)$ curves were calculated by measuring errors of ΔM for positive and negative applied fields, and averaging the ΔM errors over the range of approximately 0.1 T to 4.8 T.

The superconducting transition temperature (T_c) was also measured using an AC susceptibility technique with the amplitude of the magnetic sensing field, h, varied from 0.025 Oe to 2.2 Oe, at a frequency of approximately 4 kHz. The AC susceptibility technique provides information about primary and secondary transitions of the bulk samples. T_cs were measured on palletized samples with very small thickness. Samples were mounted onto the end of a sapphire rod and measured as the samples were warmed through the transition region at very slow rate of ~ 0.06 K/min. The T_c measurements were accurate within ≤ 0.1 K at three calibration points: liquid He at 4.2 K, liquid N_2 at 77.2 K, and room temperature. Different methods of measuring powders were tested including mounting pellets and powders placed in silicone grease, and the different methods gave the same T_c values within about 0.1 K.

RESULTS

The range of single-phase compositions determined in previous work is shown in Figure 1 [16]. All of the compositions were nominal single-phase as determined by XRD, in agreement with previous results [15], except for a small region (Ba = 2.0 and Y = 0.3 to 0.4) where sluggish reactions were suspected [16].

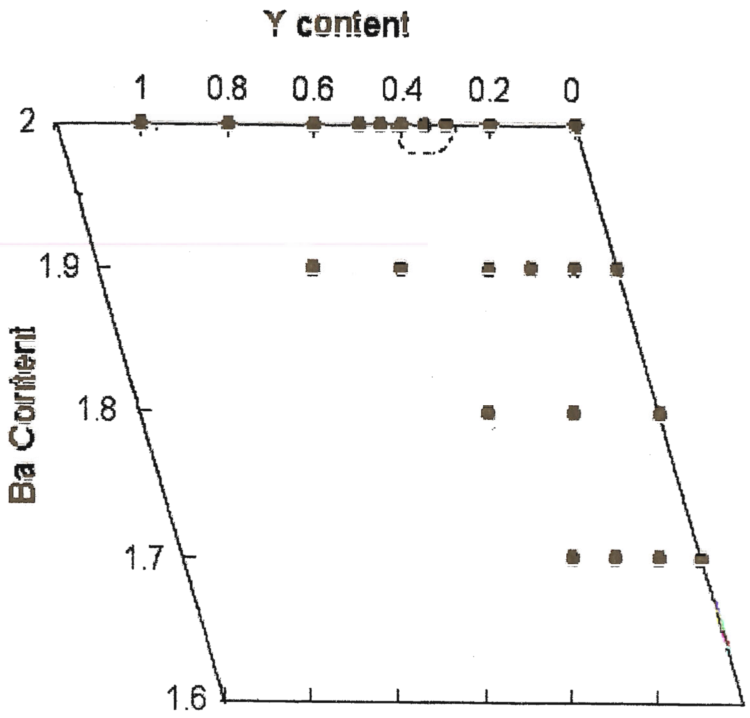

Figure 1. Compositions of $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ that were nominal single-phase, excluding Ba = 2 and Y = 0.3 to 0.4 [16].

The superconducting transitions of Ba = 2.0 and 1.9 compositions annealed only in air determined from previous work are shown in Figure 2 [16]. The transitions were broadened for Nd > 0.4, and the transition for the largest volume fraction of the powder was reduced to ~ 73 K for the Nd = 1.0 composition. A reduction and broadening of T_c for the Nd = 1.0 composition is usually observed without further processing in reduced oxygen partial pressures [15,17]. With increasing Nd and reduced Ba content, the T_c of the bulk powder is decreased, in agreement with trends reported previously for $(Y,Nd)_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ and single-phase $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ [15,17].

After annealing these compositions in 1% reduced oxygen atmosphere, the T_cs sharpened considerably and the transition onsets were greatly increased to > 92K on average, as shown in Figure 3. The increase and sharpening of T_c for the Nd-rich compositions in reduced O_2 atmosphere is consistent with previous work [7,8,15,17]. Of special note in Figure 3 is that the T_cs of the Ba = 1.9 and Nd-rich compositions were greatly increased sufficiently high so that they can be considered for practical applications.

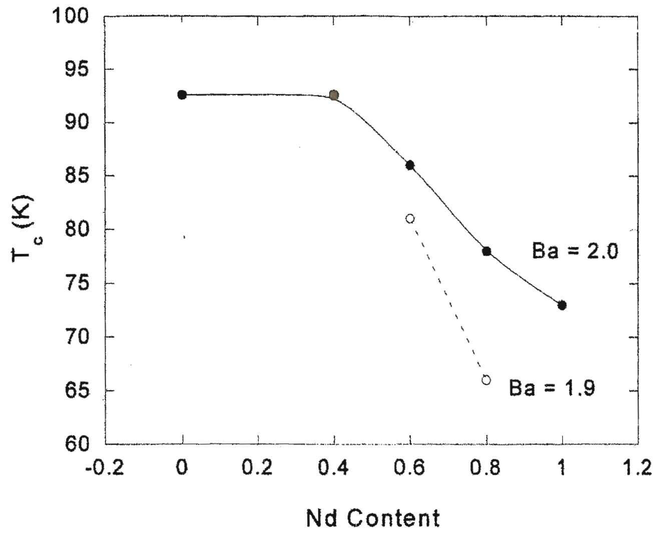

Figure 2. Transition temperature of the bulk superconducting volume fraction of powders processed in air measured by dc magnetization [16].

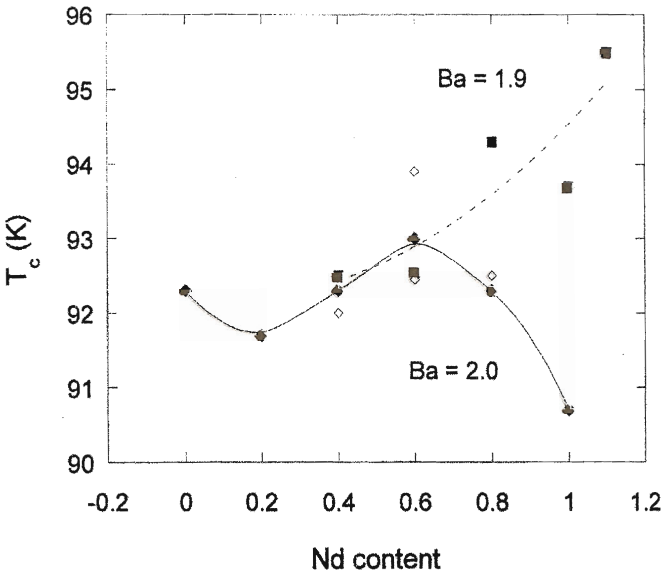

Figure 3. Transition temperature of powders processed with an additional annealing step in 1% O_2 atmosphere; Ba = 1.9 powders measured by ac susceptibility χ' onset (■) and for Ba = 2.0 powders measured by DC magnetization (◊) or ac susceptibility χ' onset (◆).

Figure 4 plots the maximum J_cs of the powders for different composition and temperature annealed only in air. In general, the J_cs decreased with increasing Nd substitution and decrease of Ba, consistent with the decrease of T_c shown in Figure 2. Only the Y123 compound had reasonably high J_c to be considered for practical applications. The normalized $J_c/J_{c\text{-max}}$ curves for the same powders is shown in Figure 5, where $J_{c\text{-max}}$ is the maximum J_c measured in the range of H_{appl} ~ (0.06 to 0.1) T. More intrinsic differences in the pinning can be observed in Figure 5.

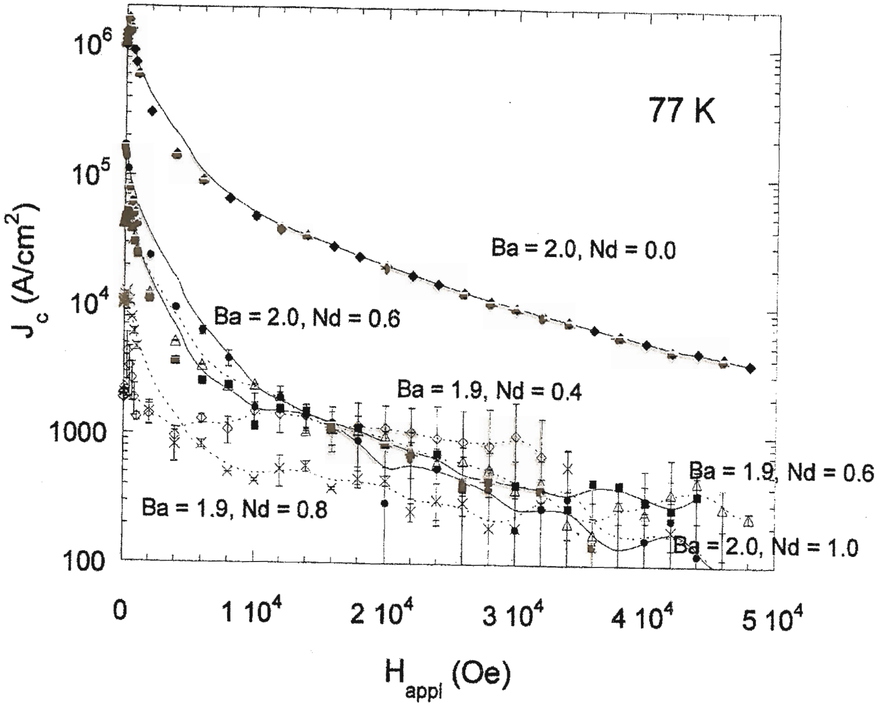

Figure 4. Critical current density as a function of applied magnetic field (H_{appl}) of powders annealed in air estimated from M-H loops for varying Nd content and Ba = 1.9 (dashed lines, open symbols) and Ba = 2.0 (solid lines, filled symbols).

The effect of the additional annealing step in 1% O_2 atmosphere is shown in Figure 6, where $J_c(H)$ curves are compared for powders processed with and without the additional step. The increase of J_c with the additional processing in 1% O_2 atmosphere can be clearly seen in Figure 6, with the J_c increased more than an order of magnitude for any applied field and all compositions. The increase is sufficiently high so that the J_cs of the Ba 1.9 compositions are about equal or better than values for Y123 material (Ba 2.0, Nd = 0), as shown in Figure 4. The

J_c of the Ba = 2.0, Nd = 0.6 compound was higher by about 50% than Y123 especially for $H_{appl} > 3$ T. Therefore these compositions might be considered for additional processing steps or for processing in thin film form to determine additional effects on flux pinning.

In Figure 7 the normalized J_c curves from Figure 6 are plotted, which gives indication of more intrinsic changes of pinning. For one composition (Ba = 1.9, Nd = 0.6), additional annealing in 1% O_2 atmosphere significantly changed the flux pinning behavior by enhancing the lower field J_cs (H< 2T) and reducing the higher field J_cs (H > 2T). The intrinsic pinning is better than Y123 as shown in Figure 5, which suggests that with additional optimization of J_c(0T) values, the absolute values of J_c could be increased substantially also. For another composition (Ba = 1.9, Nd = 0.4), the J_c was quite low for processing in air, so the normalized curve showed more usual behavior after processing in 1% O_2 atmosphere.

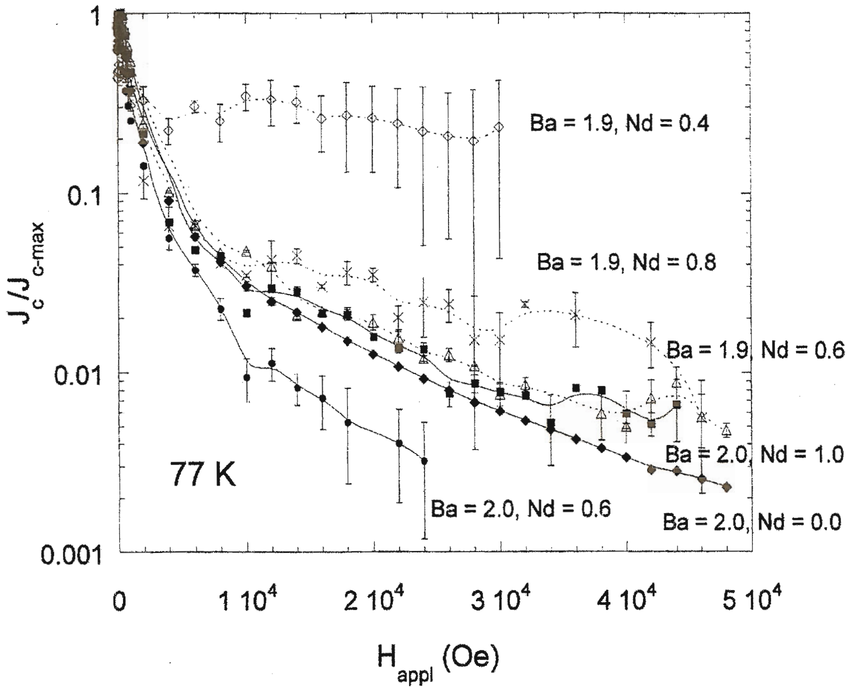

Figure 5. Normalized J_c as a function of H_{appl} for films from Figure 4; maximum J_c ($J_{c\text{-max}}$) was measured for H_{appl} ~ (0.06-0.1) T.

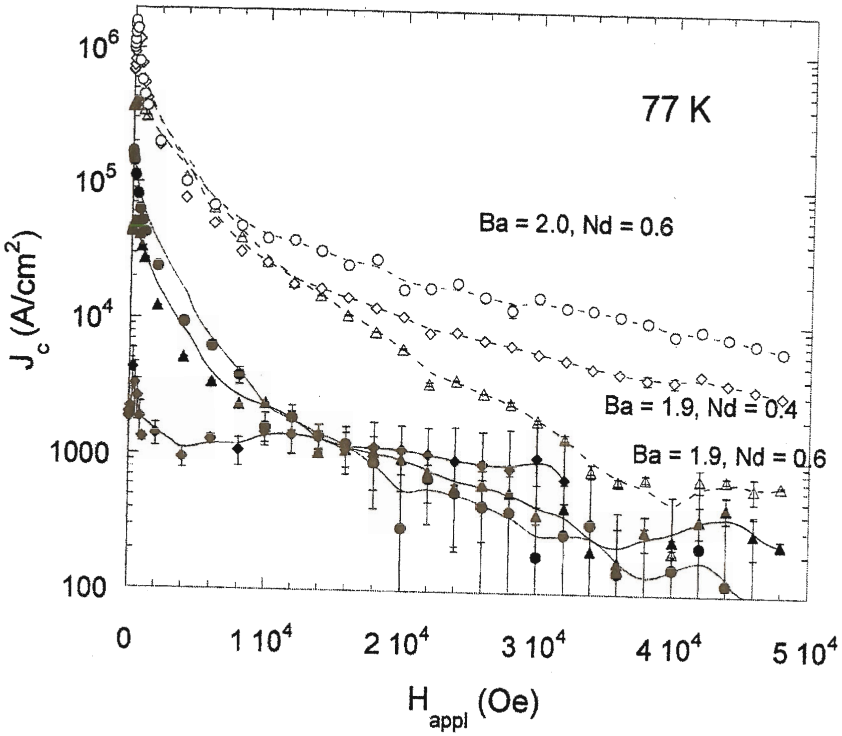

Figure 6. $J_c(H_{appl})$ comparison of powders annealed with additional step in 1% O_2 atmosphere (dashed lines, open symbols), to the same compositions annealed only in air (solid lines, closed symbols).

For all compositions 77 K, the powders showed a very small fish-tail effect, with $J_{c\text{-max}}$ occurring at 0.06 T to 0.1 T depending on composition. By comparison, the peak of maximum J_c in oxygenated melt-processed materials usually occurs around 2 to 3 T [7,8]. This suggests the powder compositions in this work are homogeneous in nature without the oxygen-deficient regions thought to cause the fish-tail effect [7,8]. A homogenous distribution of oxygen is expected as a consequence of the small size of the powders, and the near-equilibrium conditions used for processing.

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