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**CRYSTAL CHEMICAL SUBSTITUTIONS OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$
TO ENHANCE FLUX PINNING (POSTPRINT)**

T.J. Haugan, J.C. Tolliver, J.M. Evans, and J.W. Kell

**Mechanical Energy Conversion Branch
Energy/Power/Thermal Division**

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14. ABSTRACT A review of the physical properties and principles of chemical substitution of YBCO to enhance flux pinning was provided. Chemical substitution is a potential cost-effective method of introducing nano-size defections into the superconductor to provide significant enhancement of J_c . It is especially important to consider this as a method for flux pinning to achieve ultra-small defects ~1 – 4 nm in size, that were shown in this paper to be essential to realize pinning for ultra-high magnetic fields > 15 Tesla. While a significant number of studies have been done in this field, large gaps of knowledge still exist in the literature on the effect of RE substitution on J_c and pinning of YBCO. Initial studies indicate a consistent trend that substitution of 0.25 molar fraction of RE for Y or Y for RE provides significant increase of low-field J_c .					
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CRYSTAL CHEMICAL SUBSTITUTIONS OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ TO ENHANCE FLUX PINNING

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1. INTRODUCTION

Since the discovery of high temperature superconductors (HTS) in 1986 and 1987 [1,2], there has been continual interest in increasing the critical current density (J_c) of these materials in practical forms including wires, thin films and bulk materials. To increase the J_c of HTS type-II superconductors in applied magnetic fields, a well-understood method is to incorporate non-superconducting defects into the superconducting materials to act as extended pinning centers for the magnetic fluxons that penetrate the superconductor [3-5]. The size of the pinning defects is preferred to be of the order of the coherence length, which is $\sim (2-4)$ nm for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the temperature range (4-77) K. A small size of defect is sufficient to pin the vortices and also allows a higher pinning defect density to be reached. An areic density of about $H/2 \times 10^{11}$ defects/cm² is desired to pin every fluxon in an applied field of H in units of Tesla [3-5].

A conceptually simple and cost-effective method of adding nanosize pinning centers is to dope or partially introduce different elements directly into the lattice structure, which changes the properties of the localized areas in and around such doped crystal structures. The substitution of chemical elements into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO or 123) superconductor has been studied extensively and summarized for crystal growth [6], doping and physical properties [7], and materials chemistry and thermodynamics [8]. To our knowledge, the effects on flux pinning and $J_c(H)$ properties have not been compiled in a review article thus far.

This paper provides a brief review of results published in the literature on the flux pinning effects of chemical substitutions of YBCO. A major focus is examining the effect of RE substitutions for Y and/or Ba. Basic structural and physical properties of the RE and

substituted superconductors are summarized, to provide background and working database tools for studies of flux pinning of these materials. Pinning studies of materials prepared by thin film deposition, solid-state reacted powders, and melt-processed are included. Important results, trends, and peculiar findings will especially be noted.

2. BACKGROUND

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is a Cu-oxide superconductor with an oxygen deficient AB_3 perovskite structure of layered Cu-O planes interspersed with Ba and Y atoms and connected with CuO chain structures. Doping on the Y sites is easily achieved with substitution of similar ionic size lanthanide rare-earth (RE) ions, (Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Pm, Nd, Pr, Ce, La). All RE elements have stable +3 oxidation state, as does Y in the YBCO structure. Several of the elements including Ce, Pr and Tb have stable +4 states, and Eu, Sm and Yb can exist in +2 states. Ce, Pr, and Tb do not easily substitute for Y due to their preferred +4 state and smaller ionic size for those states (0.97 Å for Ce, 0.96 Å for Pr, 0.88 Å for Tb). Typically doping of Ce and Pr for Y with very small levels, < 0.1 mole fraction, is necessary before superconductivity is suppressed. Lu has also been suggested to be too small for substitution for Y. The rare-earth (RE) ionic radii sizes are close to Y, which has an ionic radius of 1.015 Å. Ionic radii of the lanthanide series range from 0.97 Å for Lu to 1.18 Å for La (Table I). Paramagnetism is evident in the RE elements, except La^{3+} , Ce^{4+} , Yb^{2+} and Lu^{3+} [7]. Partial or full substitution on the Ba site is also achieved with similar ionic radii (1.42 Å for 8-fold coordination), specifically including larger RE ions La, Pr, and Nd and Ca 2+ and Sr +2. Note also that Pm is normally not considered in studies of rare-earth substitutions because it is a synthetic element and radioactive.

3. RE-123 PHYSICAL PROPERTIES

Studies of the varying RE elements in RE123 superconductors and their properties are available in the literature for the lanthanide series: Lu [9,10], Yb [11,12], Er [13,14], Ho [15], Y [16-18], Dy [19,20], Tb [21-27], Gd [28-33], Eu [34,35], Sm [36-40], Nd [41-69], Pr [70-73], and mixtures of RE [74-141]. While review articles exist and summarize many of the physical parameters, some common properties have not been summarized for the RE ions. Table I gives physical properties of the RE123 superconductors, which are used in daily work in sample preparations and studies. Consistent trends are observed as a function of RE ion size; e.g. the melting point increases as the RE ion increases (Figure 1), and the final annealing temperature required to optimize T_c in pure O_2 atmosphere reduces steadily. Melting points of the compounds in reduced atmosphere (1%) are not as well documented mostly because of the lack of phase diagrams at such pressures. A steady increase of T_c is observed as the RE ion increases, varying from about 90 K and increasing to ~98 K for Nd123 [6].

Figure 2 plots the density of RE123 compounds, from values listed in Table I. The theoretical density of RE123 increases as the ionic radii decreases. This increase results from lattice size reduction as the ionic radii decreases, as the atomic masses do not vary significantly for the varying RE elements. The theoretical density of mixed $(\text{Y}_{1-x}\text{RE}_x)\text{123}$ is also of interest for day-to-day use in laboratory measurements. Figures 3(a-f) plots the density for several RE ions using lattice parameter studies from the literature.

Table I.

RE	Ionic Radii VIII +3 (Å) ¹⁴
Lu	0.97
Yb	0.98
Tm	0.99
Er	1.00
Ho	1.01
Y	1.01
Dy	1.02
Tb	1.03
Gd	1.04
Eu	1.05
Sm	1.06
Pm	1.07
Nd	1.08
Pr	1.09
Ce	1.10
La	1.11

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Table I. Physical and Processing Properties of $\text{RE}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$.

RE	Ionic Radii VIII, +3 ($\text{\AA}$) ¹⁴³	Melt Point in air ($^{\circ}\text{C}$) ^{92,130}	Melt Point in 1% O_2 ($^{\circ}\text{C}$) ¹³⁰	Final Anneal Temp. in 100% O_2 ($^{\circ}\text{C}$)	Tetragonal Unit Cell Lattice Parameters			Density (g/cm^3)	Source
					a (nm)	b (nm)	c (nm)		
Lu	0.977	880	-	-	0.379	0.3868	1.164	7.319	[84] [*]
					0.3787	0.3865	1.159	7.362	[84] ^{**}
Yb	0.985	900-943	862	-	0.3799	0.3873	1.165	7.268	[74]
					0.3871	0.3807	1.1658	7.2512	[11]
Tm	0.994	960	-	-	0.3810	0.3882	1.1656	7.186	[74]
Er	1.004	980	905	405 ¹⁴⁴	0.3815	0.3885	1.1659	7.154	[74]
					0.3819	0.3887	1.1677	7.132	[123]
Ho	1.015	990	-	350-440 ¹⁴⁵	0.3822	0.3888	1.167	7.106	[74]
					0.3824	0.389	1.1682	7.091	[123]
Y	1.019	1000-1010	951	435-485 ¹⁴⁵	0.3824	0.3887	1.1657	6.383	[74]
					0.3824	0.3891	1.1681	6.364	[123]
					0.382	1.1688	0.3894	6.362	[145]
Dy	1.027	1010	-	350-435 ¹⁴⁵	0.3828	0.3889	1.1668	7.071	[74]
					0.3829	0.3892	1.1692	7.049	[123]
Tb	1.040	-	-	-	0.3837	0.3837	1.1578	7.170	[26] ^{***}
Gd	1.053	1030	-	210-350 ¹⁴⁵	0.3839	0.3899	1.1703	6.961	[74]
					0.3837	0.3896	1.1688	6.980	[31]
Eu	1.066	1050	-	200-360 ¹⁴⁵	0.3845	0.3901	1.1704	6.898	[74]
					0.3851	0.3908	1.1731	6.858	[36]
Sm	1.079	1060	-	200-360 ¹⁴⁵	0.3855	0.3899	1.1721	6.860	[74]
					0.3852	0.3909	1.1719	6.846	[123]
Pm	1.093	-	-	-	-	-	-	-	-
Nd	1.109	1090	-	200-315 ¹⁴⁵	0.3855	0.3914	1.1736	6.765	[74]
					0.3869	0.3921	1.1746	6.723	[123]
Pr	1.126	-	-	-	0.3922	-	-	6.593	[74]
					0.3845	1.1801	0.3905	6.730	[145]
Ce	1.143	-	-	-	0.3838	0.3885	1.1651	6.856	[146] ^{***}
La	1.160	1090	-	-	0.3856	0.3906	1.1783	6.700	[74]

*Lattice parameters for $\text{LuBa}_{1.6}\text{Sr}_{0.4}\text{Cu}_3\text{O}$ **Lattice parameters for $\text{LuBa}_{1.5}\text{Sr}_{0.5}\text{Cu}_3\text{O}_7$ ***Lattice parameters of $\text{TbSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7+x}$ ****Partial (1/4) substitution for Y: 85.8% Y123, 5% BaCuO_2 , 5% BaCeO_3

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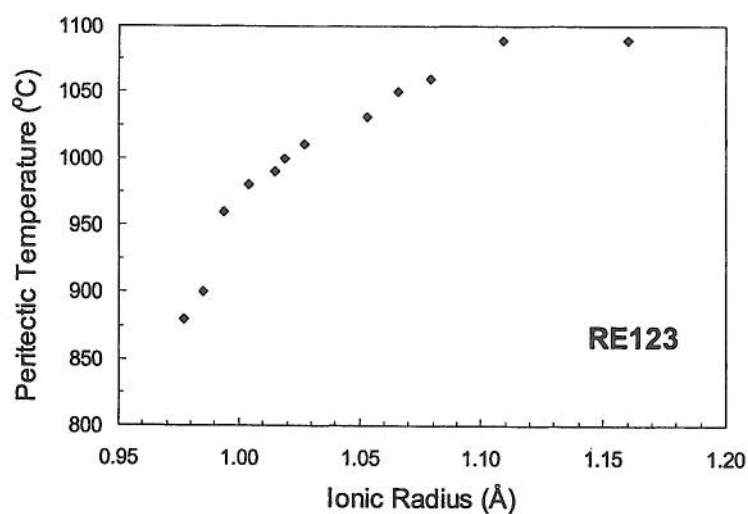


Figure 1. Peritectic decomposition (melting) temperature in air for RE123 compounds (Table I).

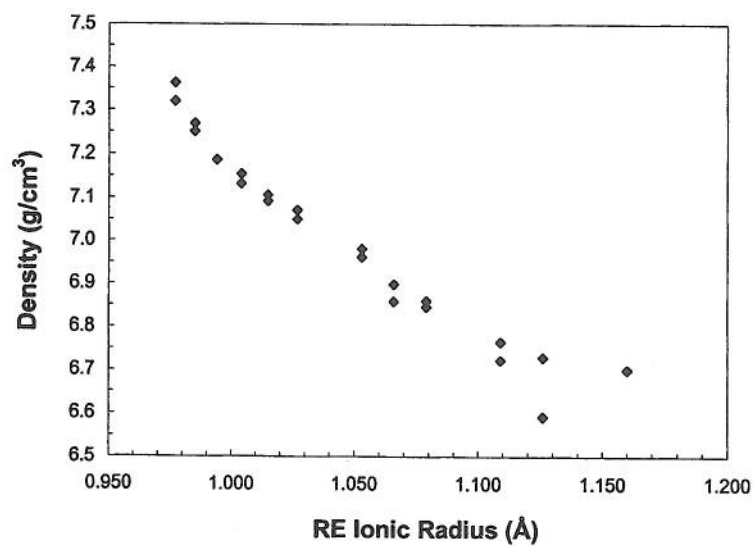


Figure 2. Theoretical density of RE123 from values listed in Table I.

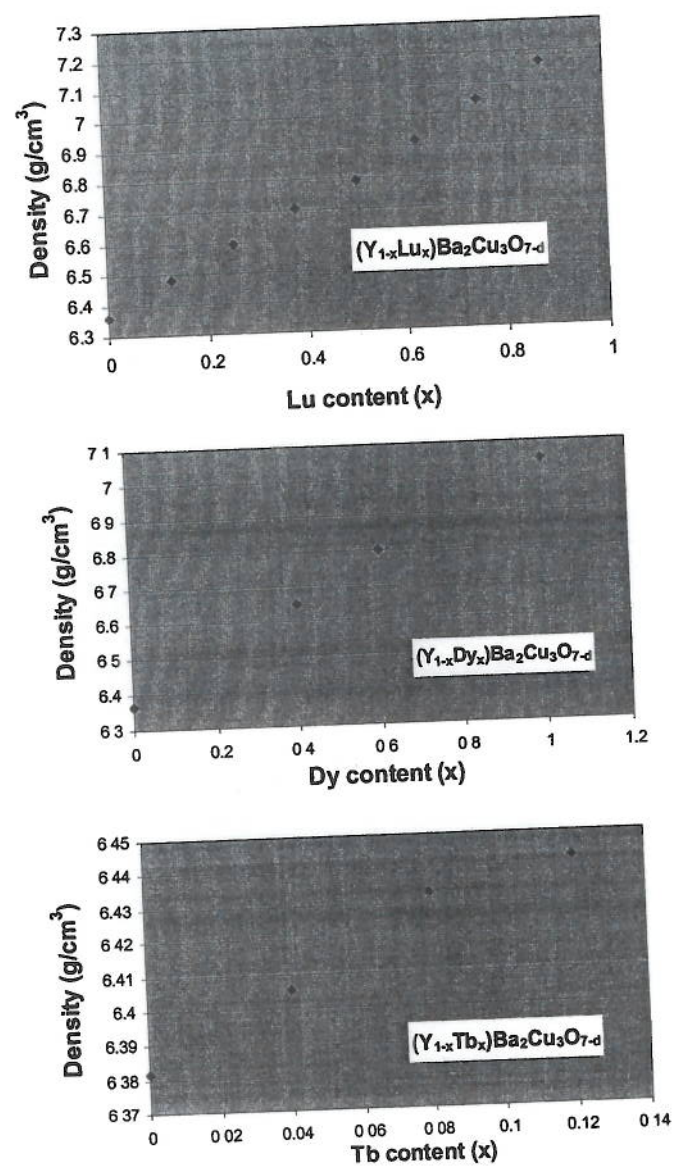


Figure 3(a-c). Theoretical density of (RE,Y)123 as a function of RE partial substitution; (a) top for (Lu,Y)123 [9], (b) middle for (Dy,Y)123 [20], (c) bottom for (Tb,Y)123 [27].

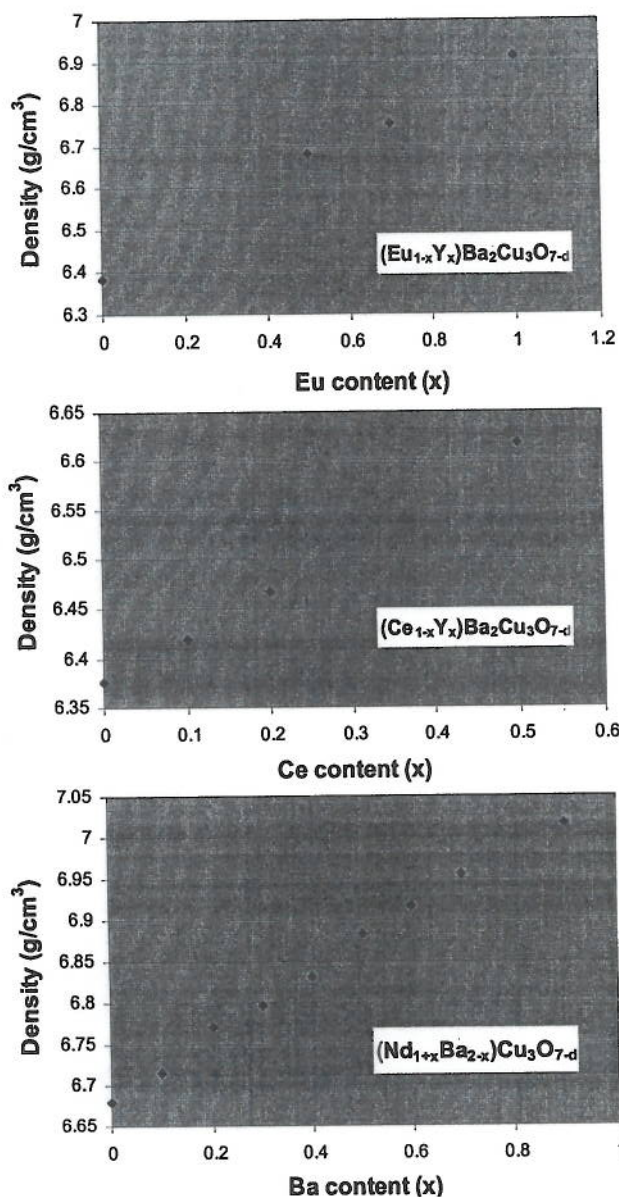


Figure 3(d-f). Theoretical density of (RE,Y)123 for partial substitution of Y and Ba; (d) top for (Eu,Y)123 [115,35], (e) middle for (Ce,Y)123 [75], and (f) lower for (Nd,Y)123 [93].

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The use of reduced atmosphere processing is especially critical for the larger RE ions or mixtures with these ions, which prevents partial substitution of these RE ions for Ba [68,69,105,131]. Partial substitution generally reduces T_c far enough to degrade or eliminate use at 77K. For example, Figure 4 compares T_c measurements of (Y,Nd)123 mixtures processed with a final high temperature annealing in air versus 1% oxygen [69]. Powders processed in air or 1% oxygen had similar X-ray patterns, however markedly different T_c s as shown in Figure 4, as well as J_c s [68,69]. Similarly, other authors have observed differences of superconductivity for the large RE ions, comparing processing in air versus reduced oxygen atmospheres [105,131].

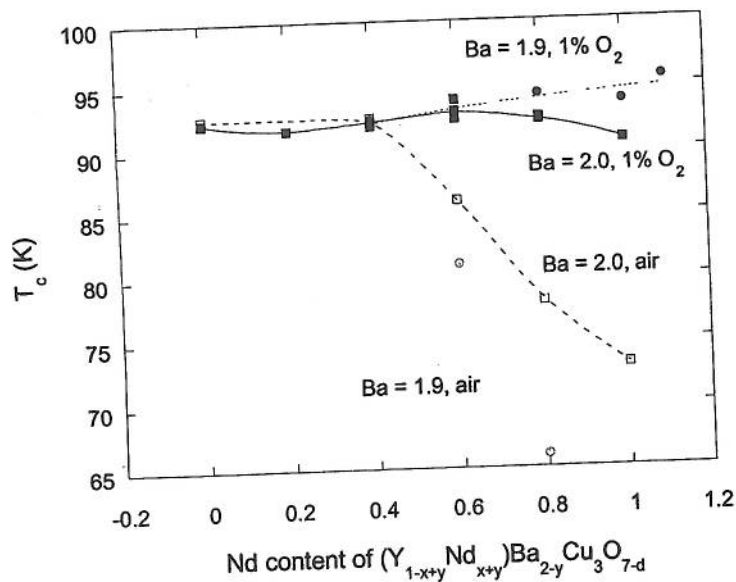


Figure 4. T_c versus of $(Y_{1-x+y}Nd_{x+y})Ba_{2-y}Cu_3O_{7-d}$ composition powders prepared by solid state reaction: high temperature annealing in air (open symbols), and high temperature annealing in 1% O_2 atmosphere (closed symbols) [69].

3. FLUX PINNING OF CHEMICALLY SUBSTITUTED DEFECTS

Chemical substitution on the ionic sites of the RE unit-cell produces both localized and macroscopic structures that are partially or fully non-superconducting, depending on variables such as the molar fraction substitution, chemical element, and others.

A primary question when considering substitutions is whether they achieve uniform dispersions, or if there is segregation and/or coalescence of alternate-phase material throughout the composite. Figure 5 illustrates several possible microstructures of the material for same composition mixtures. Many additional variations of microstructures and

orientations are also conceivable; for example, phases can form as aggregates of various sizes and size distributions or in columnar structures. The variation of microstructures are expected to cause variations of microscopic strain surrounding the Y123 superconductor regions. In addition to localized strains, macroscopic strains are expected from the stress on the entire composite from volume fraction additions of non-lattice matched, non-superconducting materials.

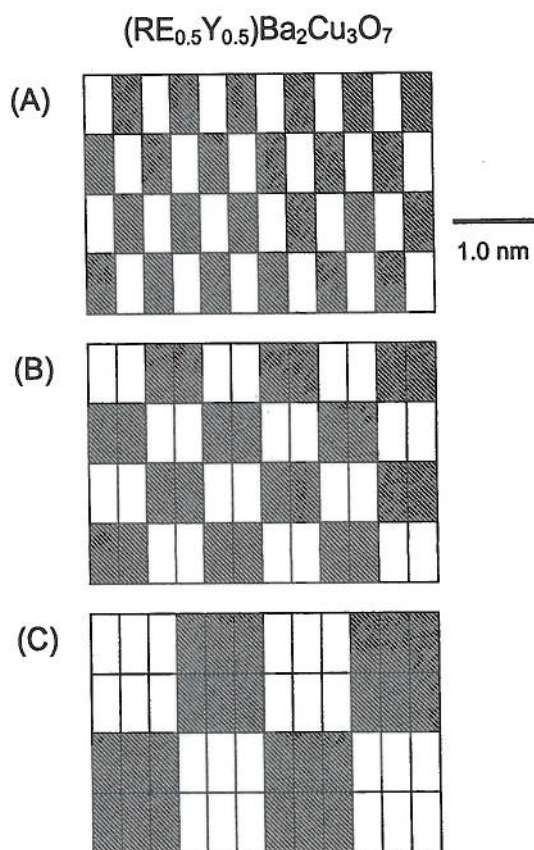


Figure 5. Schematic representation of possible microstructures of $(\text{Y}_{0.5}\text{RE}_{0.5})\text{Ba}_2\text{Cu}_3\text{O}_{7.3}$ superconductors represented by unit cells (rectangles); shaded unit cells = RE123, open cells = Y123; note unit cells are not exact size. Different orientations and microstructures are conceivable, depending on processing kinetics and parameters.

The effects of microscopic strains from unit cell mismatches have been studied by several authors using simple models for unit cell aggregate distributions. In one study, varying (RE,Y)123 unit cell mismatches were examined, and a difference of pinning strength of > 300% for varying rare-earth was predicted [128]. An (Eu,Y)123 mix was theorized to have optimal pinning strengths, in rough agreement with experimental measurements of various (RE,Y) mixed powders prepared by solid-state reaction [128].

The distribution of strains in the composites can be observed to some degree with X-ray diffraction (XRD), as shown in Figure 6 for $(Y_{0.6}Nd_{0.4})_{123}$ mixtures prepared by thin film deposition [147]. As seen in Figure 6, the XRD peaks for the 003 reflection were quite broad indicating a range of unit cells d-spacings that result presumably in different strains on the Nd123 and Y123 unit cells. Some substitution of Nd on the Ba site is also expected for these films.

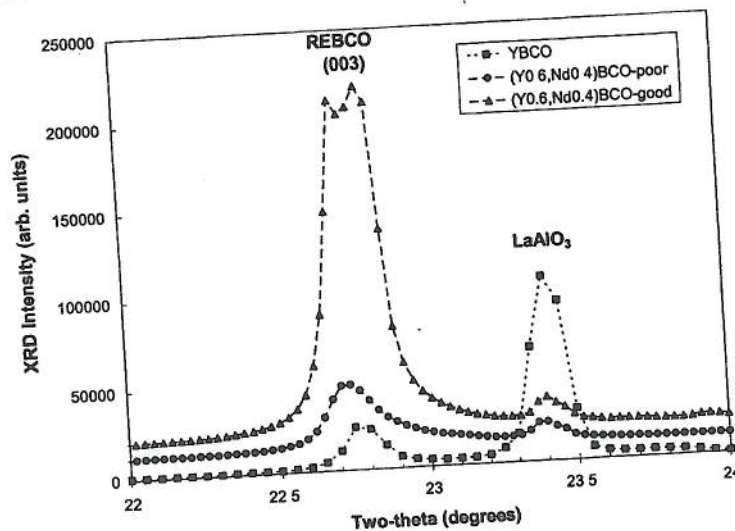


Figure 6. X-ray diffraction of $(Y_{0.6}Nd_{0.4})Ba_2Cu_3O_{7.8}$ composition films prepared with good c-axis orientation (solid circles), with mixed c-axis and a-axis orientation (solid triangles), and compared to a 123 film prepared by pulsed laser deposition (solid squares) [147].

In addition to localized strain variations, chemical substitution can also affect the T_c of localized regions surrounding doped areas from diffusion and reactions. A sharp interface between insulator and superconductor is desired to maximize pinning strength, however for chemically substituted defects some gradations of T_c are expected especially for elemental substitution of highly reactive materials. The effect of chemical substitutions on T_c have been summarized by Skakle [7].

As illustrated in Figure 5, an important aspect of chemical substitution is that the size of the defect can be reduced as small as ~1nm, the size of the unit cell. Such an ultra-small pinning defect can allow very high pinning defect densities to be achieved, and therefore have potential to pin very high magnetic fields. Table II calculates the defect number densities and

the equivalent pinning fields for those defects that can be achieved by reducing the size of defect to $\leq 8 \text{ nm}^3$. Values in Table II were calculated assuming every defect can pin individual fluxons that enter the superconductor, and that dispersions of point-like defects provide effective pinning structures. Initial studies demonstrate that dispersions of nanoparticles $\sim 8 \text{ nm}$ diameter in YBCO provide significant increase of $J_c(H)$ [148,149].

Table II demonstrates several important trends. (1) By reducing the defect size to the order of $\sim 2 \text{ nm}$, the volume fraction can be reduced as low as (0.1-0.3)% to pin fields up to (5-10) T. Therefore even small volume fraction additions can be considered for very effective pinning. This indirectly suggests that precise control of the composition is necessary to control pinning, and that careless laboratory practices might accidentally produce significant pinning without knowledge of the controlling factors. (2) To achieve pinning for high fields $> 15 \text{ T}$, the defect size must be reduced to $\sim 4 \text{ nm}^3$ or less to keep the volumic fraction of defects $< 20\%$; i.e. the defect size must be reduced significantly to pin the very close-proximity fluxons that penetrate the superconductor in high magnetic fields.

Table II. Defect number densities required to reach (one defect/fluxon) for varying applied magnetic fields, as a function of defect size.

$H_{\text{appl}}(\text{T})$	Linear Defect Density (#/100nm)	Areic Defect Density (#/100nm ²)	Volumic Defect Density (#/100nm ³)	1nm ³ Defects, Volumic Fraction (%)	2nm ³ Defects, Volumic Fraction (%)	4nm ³ Defects, Volumic Fraction (%)	8nm ³ Defects, Volumic Fraction (%)
5	5.0	25.0	125	0.01	0.1	0.8	6.4
10	7.1	50.0	354	0.04	0.3	2.3	18.1
15	8.7	75.0	650	0.06	0.5	4.2	33.3
20	10.0	100.0	1000	0.10	0.8	6.4	51.2
25	11.2	125.0	1398	0.14	1.1	8.9	71.6

4. CRITICAL CURRENT DENSITY OPTIMIZATION

One of the goals for chemical substitution is to increase low or self-field J_c s which are controlled by pinning properties and important for power transmission applications. Maintaining high $J_c(\text{self-field})$ is also important to realize improvements of pinning at higher fields; for example we have observed this phenomenon in processing Y123 films prepared with Y_2BaCuO_5 nanoparticle additions [148,149]. However this is not an absolute rule, as different trends can be observed, particularly if the $J_c(\text{low-field})$ values are orders of magnitude lower [68,69].

Table III gives the $J_c(\text{low-field})$ properties of RE substituted Y123 compounds prepared by different processing methods. As seen in Table III, a large number of rare-earth compounds have not been systematically studied for RE substitution (to our knowledge). Also the processing conditions are different for each material, which makes it difficult to provide a direct comparison of results. Despite these differences, however, Table III indicates that many of the RE compositions show improvement of J_c with RE substitution, varying depending on the RE ion and the amount of substitution.

Table III. Critical current density as a function of RE substitution in $(Y_{1-x}RE_x)123$.

(Y,RE) 123	Process Method	Ionic Radii (Å) VIII CN, +3	x	J_c (MA/cm ²)	Comments	Reference
Lu		0.977				
Yb		0.985				
Tm		0.994				
Er		1.004				
$Y_{1-x}Ho_x$	Sputter films	1.015	0.000	0.210	J_c at 0.1 T	[98]
			0.200	0.350		
			0.400	0.680		
			0.700	0.290		
			1.000	0.190		
Y		1.019				
$Y_{1-x}Dy_x$	PLD films	1.027	0.000	0.300		[19]
			0.200	2.800		
			0.400	2.300		
			0.600	0.850		
			0.800	3.800		
			1.000	0.430		
$Y_{1-x}Tb_x$	powder	1.040	0.000	0.011		[82]
			0.200	0.008		
$Y_{1-x}Gd_x$	sputter films	1.053	0.000	0.220	J_c at 0.05T	[28]
			0.200	0.700		
			0.400	1.150		
	powder		0.000	1.000	J_c -norm for $x=0$	[115]
			0.100	1.380		
			0.200	1.430		
			0.300	1.730		
			0.400	1.270		
			0.500	1.360		
			0.600	1.320		
			0.700	1.520		
			0.800	1.360		
			0.900	1.410		
			1.000	1.270		

(Y,RE) 123	Process Method	Ionic Radii (Å) VIII CN, +3	x	J_c (MA/cm ²)	Comments	Reference
$Y_{1-x}Eu_x$	MTG ?	1.066	0.000	0.027		[128]
			0.200	0.053		
			0.300	0.056		
			0.500	0.030		
			0.700	0.040		
			0.800	0.033		
			1.000	0.020		
Sm		1.079				
Pm		1.093				
$Y_{1-x}Nd_x$		1.109	0.100	0.043	J_c = arb. units	[108]
			0.170	0.069		
			0.270	0.021		
			0.400	0.043		
$Y_{1-x}Pr_x$		1.126	0.000	0.010		[90]
			0.080	0.004		
Ce		1.143				
La		1.160				

The variation of J_c with RE substitution is also plotted in Figure 7 for several of the RE ions from Table III. Figure 7 suggests a general trend that doping with RE mole fractions of either around 0.25 or 0.75 enhances low-field J_c values. The mechanism for improvement is presumably similar for substitution of RE for Y, or vice-versa, and suggests that stress-induced pinning from dissimilar lattice unit cells can be result in J_c enhancement [88,128].

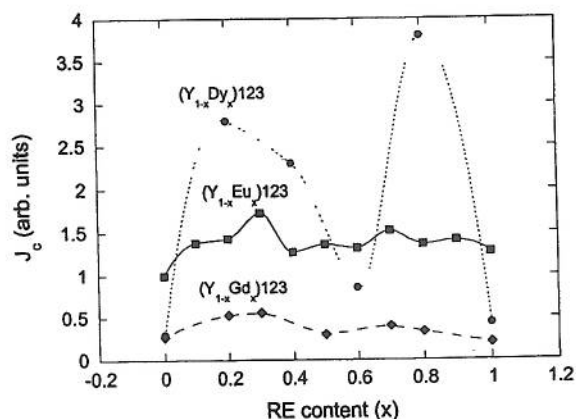


Figure 7. Effect of RE substitution on J_c (low-field) of $(Y_{1-x}RE_x)123$ from Table III.

4.1 Tb SUBSTITUTION FOR Y IN Y123

Terbium is unique among the rare earth elements when used to substitute for yttrium in $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ (Y-123). When used to replace Y in Y-123, $\text{TbBa}_2\text{Cu}_3\text{O}_{7-d}$ (Tb-123) does not form due to strong chemical intermixing between the Tb and Ba resulting in a BaTbO_3 phase [23,25,26]. However, more recent research has shown that while the standard 123 phase cannot be formed due to Ba interactions, a similar 123 phase can be formed with the composition $\text{TbSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_7$. This 123 phase can be formed by substituting Sr for Ba and a small amount of Mo for Cu in order to reduce the Sr-Cu interaction and has a superconducting onset temperature of 80K [21].

It has been reported that terbium can be substituted into Y-123 to form $\text{Y}_{1-x}\text{Tb}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-d}$ (Y,Tb-123) with $x < 0.75$ in thin films and still maintain phase purity [23]. Two important properties have been noted from studies dealing with Y, Tb-123. First, there is no appreciable change to the critical temperature for superconductivity, and second, the critical current density does not change significantly [22,24,82]. This leads to debate as to the valence of Tb in 123 phases due to the mixed valence state of Tb in the oxide form Tb_4O_7 . The 2 valence states of Tb in the oxide +3 and +4 and the presence of the +4 state were originally believed to be the cause of the failure of Tb-123 to form. However, recent research has shown that Tb is in a +3 state when in the Y-123 phase ($L_{3\text{-edge}}$ XANES studies) and is not hybridized [23].

4.2 Ce SUBSTITUTION FOR Y IN Y123

Ce is one of three rare earths that cannot form the phase $\text{REBa}_2\text{Cu}_3\text{O}_{7-d}$, with the other two being Pr and Tb. Also, Ce will not form a 123 phase in Sr doped materials. This is because the $\text{CeBa}_2\text{Cu}_3\text{O}_{7-d}$ phase is inhibited due to the Ce ion preferring a tetravalent state within the 123 structure [7,21]. However, it is possible to replace Y with Ce in Y-123 films to form $\text{Y}_{1-x}\text{Ce}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-d}$ with $x < 0.3$. Overall, the behavior of Ce is similar to that of Pr in that as the Ce concentration increases, the normal resistivity increases, and the T_c decreases. However, the mechanism for the reduction of T_c in Ce doped Y-123 is different from that of Pr and is due to the preferred +4 valence state of Ce ions [23].

SUMMARY

A review of the physical properties and principles of chemical substitution of YBCO to enhance flux pinning was provided. Chemical substitution is a potential cost-effective method of introducing nano-sized defects into the superconductor to provide significant enhancement of J_c . It is especially important to consider this as a method for flux pinning to achieve ultra-small defects $\sim 1\text{-}4$ nm in size, that were shown in this paper to be essential to realize pinning for ultra-high magnetic fields > 15 Tesla. While a significant number of studies have been done in this field, large gaps of knowledge still exist in the literature on the effect of RE substitution on J_c and pinning of YBCO. Initial studies indicate a consistent trend that substitution of 0.25 molar fraction of RE for Y or Y for RE provides significant increase of low-field J_c .

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