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Fe Site Occupancy and Superconductivity in $Y_{1-z}Ca_zBa_z(Cu_{1-x}Fe_x)_3O_{6+y}$

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Fe SITE OCCUPANCY AND SUPERCONDUCTIVITY IN $Y_{1-z}Ca_zBa_z(Cu_{1-x}Fe_x)_3O_{6+y}$

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The structure, superconducting transition temperature T_c and Fe site occupancy in $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ depend on annealing conditions and x. The maximum solubility of Fe in this compound is $x \approx 0.16$ with Fe primarily (94%) on the Cu (1) chain site when prepared conventionally. Synthesis of $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ under high temperature reducing conditions followed by low temperature oxygenation results in greater occupancy of the Cu (2) plane site and regions of Fe clusters in the Cu (1) plane. In this paper we show that the partial substitution of Ca for Y results in larger Fe occupancy of the Cu (2) site when prepared conventionally. $Y_{1-z}Ca_zBa_z(Cu_{1-x}Fe_x)_3O_{6+y}$ prepared under reducing conditions has 81% of the Fe dopant on the Cu (2) site.

Materials $Y_{1-z}Ca_zBa_z(Cu_{1-x}Fe_x)_3O_{6+y}$ ($0.05 \leq z \leq 0.15$, $0.003 \leq x \leq 0.20$) were prepared from the solid state reaction method. Method I samples were annealed in flowing O_2 and Method II samples were annealed in flowing N_z followed by a low temperature anneal in flowing O_2. Phase purity was determined by x-ray diffraction. Superconducting transition temperature were obtained by magnetic susceptibility data. Fe site occupancy was determined by ^{57}Fe Mössbauer spectroscopy. All the materials were single phase and could be fit to the $YBa_2Cu_3O_{6+y}$ unit cell. The partial substitution of Ca for Y allows for greater solubility of Fe (up to $x = 0.20$ For $z = 0.05, 0.10$), though the latter samples were not superconducting. T_c of the Ca substituted samples, for a given x, is slightly less than that observed in $YB_z(Cu_{1-x}Fe_x)_3O_{6+y}$. Mössbauer spectroscopy showed that up to 51% of the Fe dopant occupies the Cu (2) site in materials prepared by Method I. Materials prepared by Method II show higher occupancy, up to 81%, and depressed T_c's compared to samples prepared by Method I. The decrease in T_c with increasing Fe occupancy of the Cu (2) site is probably due to changes in microstructure and Fe magnetic pair breaking effects.

Fe SITE OCCUPANCY AND SUPERCONDUCTIVITY IN $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$

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X-ray diffraction and ^{57}Fe Mössbauer spectroscopy studies show that partial substitution of Ca for Y in $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ $(0.05 \le z \le 0.15, 0.003 \le x \le 0.20)$ result in increased Fe solubility and a larger percentage of Fe occupancy of the Cu(2) plane site (prepared conventionally). Materials with $z > 0.00$ have a slightly depressed superconducting transition onset temperature T_c relative to the $z = 0.00$ compounds. It is also shown that Fe occupancy of the Cu(2) site in $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ can be substantially increased when these materials are treated at high temperatures in inert atmospheres followed by oxygenation at low temperatures. T_c decreases more rapidly in these latter materials compared to the conventionally prepared ones. Implications concerning ordered Fe cluster formation and superconducting pair breaking in the Cu(2) site are drawn.

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INTRODUCTION

The structure, superconducting transition temperature T_c and Fe site occupancy in $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ depend on annealing conditions and x.[1,2] The maximum solubility of Fe in this compound is $x \approx 0.16$ with Fe primarily ($\approx$ 94 %) occupying the Cu(1) chain site in multifold oxygen coordination when prepared conventionally (sintering at 925°C followed by an anneal at 350°C in O_2). The Fe dopant results in an orthorhombic-to-tetragonal transition (near x = 0.06) and depresses T_c. However, orthorhombic materials having increased T_c's with values of x as high as 0.15 can be prepared by annealing the materials in a reducing atmosphere followed by a low temperature anneal in O_2.[1,2] These materials have a larger percentage ($\approx$ 27%) of the Fe occupying the Cu(2) plane site (recently confirmed by neutron diffraction[3]) and form regions of Fe-clusters in the Cu(1) plane.

In this paper we explore the possibility of further chemically driving the Fe dopant to the Cu(2) site by partial substitution of Ca for Y. Manthiram et al.[4] have shown that the partial substitution of Ca for Y in $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}$ results in a lower value of the total oxygen stoichiometry ($6 + y = 6.87$ for $z = 0.1$ at 350°C in O_2). It has been argued[1,2] that oxygen depletion of the Cu(1) site drives Fe to the oxygen-rich Cu(2) site in $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$. Therefore, $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($z > 0.00$) with yet lower y was expected to have a larger percentage of Fe occupying the Cu(2) site (prepared conventionally). This is confirmed by ^{57}Fe Mössbauer spectroscopy in the present work. We also show that by annealing $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ under reducing conditions at elevated temperatures, up to 81% of the Fe dopant can occupy the Cu(2) site.

EXPERIMENTAL

The materials $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($0.05 \leq z \leq 0.15$, $0.003 \leq x \leq 0.20$) were prepared by the solid state reaction method. Stoichiometric amounts of dried Y_2O_3, $CaCO_3$, $BaCO_3$, CuO, and Fe_2O_3 were ground with a mortar and pestle and pressed into a pellet. Fe_2O_3 enriched with ^{57}Fe isotope (92.3%) was used for the $x \leq 0.06$ samples to enhance the Mössbauer effect. The initial treatment consisted of annealing in air or O_2 at 925°C for 105 to 115 h with 3 or 4 intermediate grindings and pressings. Portions of these samples were then treated in several different ways. The conventional (method I) treatment involved annealing the sample in flowing O_2 at 400°C for 16 h with slow cooling to room temperature. In method II we annealed the sample at 700°C in flowing N_2 for 24 h, slow cooled to 350°C in N_2, turned off the N_2 and exposed the sample to flowing O_2 for 8h. The sample was then slow cooled in flowing O_2 to room temperature. The third method (method III) involved annealing the sample at 700°C in flowing N_2 for 24 h with slow cooling to room temperature.

X-ray diffraction was performed using Cu Kα radiation. Typical errors in reported lattice parameters are 0.007 - 0.010 Å. Superconducting transition temperatures T_c were determined as the onset of diamagnetism from magnetic susceptibility data obtained in an applied magnetic field of 100 gauss using a SQUID magnetometer. Mössbauer spectroscopy was performed at room temperature with a constant acceleration spectrometer using a ^{57}Co-Rh source. Absorbers were made by grinding the samples into fine powder, mixing with sugar and enclosing the mixture in a plastic sample holder. Typical absorber thickness was 0.01-0.02 mg ^{57}Fe/cm^2. Isomer shifts are reported relative to Fe metal at room temperature.

RESULTS

X-ray diffraction showed that all materials were single phase. The powder patterns are in accord with the $YBa_2Cu_3O_{6+y}$ unit cell. Lattice parameters and T_c for materials prepared by method I (conventional synthesis) are given in Table I. The partial substitution of Ca for Y allows for greater solubility of Fe in $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$, up to x = 0.20 for z = 0.05 and 0.10, though, these latter samples are not superconducting. T_c of the Ca substituted samples, for a given x, is slightly less than that observed in $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$.

Mössbauer spectra of $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ were fit

3 or 4 symmetric quadrupole doublets. In Table II we summarize the ranges of isomer shifts (IS), quadrupole splittings (ΔE_Q) and full width at half maximum line widths (FWHM) of the subspectra observed in materials prepared by method I of this work. Previously we have assigned subspectra A, B, and D to Fe substitution at the Cu(1) site in 4-fold planar, 5-fold pyramidal and 4-fold tetrahedral oxygen coordination, [denoted (1)4, (1)5 and (1)4t] respectively, and subspectra C to Fe substitution at the Cu(2) site in 5-fold pyramidal oxygen coordination [denoted (2)5].[1] Clearly, Fe occupancy of the Cu(2) site has increased with the partial substitution of Ca for Y. In Table III we show the fitted % subspectra areas of $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ prepared by method I for different values of z and x. The z = 0.15 x = 0.003 sample has an additional quadrupole site, denoted E. This subspectrum has previously been observed by Blue et al.[6] and was attributed to Fe at the Cu(2) site.

We also treated $Y_{.90}Ca_{.10}Ba_2(Cu_{1-x}Fe_x)_3O_{6+y}$ (x = 0.01, 0.06 and 0.10) by method II. In Table IV we show lattice parameters, T_c and the percentage of Fe dopant occupying the Cu(2) site (determined by Mössbauer spectroscopy) of these samples. Comparison of these data with the ones of the z = 0.10 samples prepared by method I (Table I) shows that materials with greater Fe occupancy of the Cu(2) site have a lower T_c. This fact is also borne out by the lower T_c's of the z = 0.05 samples (see Table I) which have an already abnormally high Fe occupancy of the Cu(2) site (see Table IV) when synthesized by method I.

Mössbauer spectra of $Y_{.90}Ca_{.10}Ba_2(Cu_{0.997}Fe_{0.003})_3O_{6+y}$ prepared by method III could be fit to 3 quadrupole doublets A, C, and C*, where C* is a doublet previously not seen by us. It has hyperfine parameters IS = 0.305(7) mm/s, ΔE_Q = 1.00(9) mm/s and FWHM = 0.24(3) mm/s, and occupies 46% of the spectral area. Quadrupole doublets A and C occupy 33 and 21% of the spectral area, respectively. Upon oxygenation, subspectra C* transforms to C with 67(1)% of the spectral area and subspectra A transforms to B with 33(1)% of the spectral area. A sample with slightly more Ca, $Y_{0.85}Ca_{0.15}Ba_2(Cu_{0.997}Fe_{0.003})_3O_{6+y}$, treated by method III could be fit to three quadrupole doublets, A, C and C*, occupying 19%,72% and 9% of the spectral area, respectively.

Finally we note that no Fe-doped impurity phases such as CuO, $BaCuO_2$, Y_2BaCuO_5, $CaFeO_3$ or Fe_2O_3 appear in the Mössbauer spectra of any of our samples.

DISCUSSION

The aims of this study to achieve increased site selective Fe substitution on the Cu(2) site were indeed achieved in the partly substituted Ca materials. We assume that the lower oxygen content of these materials, especially at elevated temperatures, drives Fe into the higher oxygen coordinated Cu(2) position. These effects are enhanced through the special preparation protocols (methods II and

III) and presumably can be further optimized. In this paper we report a preparation with 81% of Fe on the Cu(2) site, but practically exclusive occupation should also be achievable. These samples are of special interest for a variety of reasons including the effects of Fe on T_c.

In this respect the strong T_c depressions observed in this study are markedly different from increases observed in T_c earlier[1,2] in the $z = 0.0$ materials. A variety of influences have to be considered in this connection. To begin with, $x = 0.0$ materials already show a small decrease in T_c with z and a further dependence on y has to be expected. However, we assume that the major contributions to the marked decrease in T_c are changes in microstructure and concomitant Fe superconducting pair breaking. Previous Mössbauer studies[1,2] (in $z = 0.0$ materials) have indicated that under reducing conditions Fe segregations can occur along what are probably relatively ordered domain walls separating orthorhombic cells. In particular, our diagnosis[1] for the increased local environment (1)5 (in reoxygenated samples) is an argument in this direction. These oxygen starvation-Fe clusters will imprint a similar microstructure in the Cu(2) plane through bond sharing with O. This leaves the bulk of the samples relatively Fe free, explaining their relatively unchanged T(c) (from $YBa_2Cu_3O_{6+y}$) and orthorhombic crystal structure.

The much greater T_c depression of the $z > 0.00$ materials indicates a somewhat different microstructure. In particular, we assume that Fe is more randomly distributed in Cu(2) due to the probable disorder between Y and Ca and the concomitant bond disorder. We expect Fe^{3+} to seek proximity with Ca^{2+} on a valence equalizing principle. Therefore, these materials sense a larger influence of the pair breaking effects of the more randomly distributed Fe. In fact, a direct comparison of the present data with values from Zn substituted materials[7], taken at face value, suggests a stronger T_c depression per atom for Fe compared to Zn substituted on Cu(2).

We want finally to mention that quadrupole site C*, which is observed in O-depleted $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ (z = 0.10,0.15 and x = 0.003) prepared by method III, is something of an anomaly. Presently we attribute it to Fe substitution at the Cu(2) site with a Ca^{2+} nearest neighbor. We note that, generally, subspectrum C is magnetically split at room temperature in O-depleted $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ due to antiferromagnetic ordering of the Cu(2) sites. This is observed in O depleted $Y_{0.95}Ca_{0.05}Ba_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$, however, it is not observed in materials richer in Ca (z = 0.10, 0.15). The partial substitution of Ca^{2+} for Y^{3+} dopes holes into the system and moves the system away from the antiferromagnetic state towards the superconducting state. Mössbauer measurements below room temperature are currently underway to determine the antiferromagnetic ordering temperature of oxygen-reduced (method III) $Y_{1-z}Ca_zBa_2(Cu_{0.997}Fe_{0.003})_3O_{6+y}$ (z = 0.10 and 0.15).

CONCLUSIONS

$Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ prepared conventionally or by reduction in inert atmospheres show greater Fe occupancy of the Cu(2) plane site and larger Fe solubility than conventionally prepared $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$. T_c decreases with increasing Fe occupancy of the Cu(2) site, probably due to changes in microstructure and Fe magnetic pair breaking effects.

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Table I. Lattice parameters and T_c for $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ synthesized by method I.

z	x	a_0(Å)	b_0(Å)	c_0(Å)	T_c(K)
0.00[a]	0.003	3.832	3.889	11.67	93(1)
	0.03	3.855	3.871	11.66	85(1)
	0.06	3.867	3.867	11.69	69(1)
	0.10	3.865	3.865	11.67	55(1)
	0.15[b]	3.867	3.867	11.65	0
0.05	0.003	3.825	3.900	11.68	89(1)
	0.01	3.829	3.904	11.70	87(1)
	0.06	3.876	3.876	11.73	51(1)
	0.10	3.876	3.876	11.70	19(1)
	0.15	3.887	3.887	11.68	0
	0.20	3.897	3.897	11.69	0
0.10	0.003	3.829	3.890	11.69	85(1)
	0.01	3.827	3.891	11.66	86(1)
	0.06	3.847	3.859	11.66	67(1)
	0.10	3.876	3.876	11.73	39(1)
	0.15	3.897	3.897	11.67	0
	0.20	3.882	3.882	11.65	0
0.15	0.003	3.838	3.883	11.72	86(1)
	0.01	3.830	3.886	11.72	85(1)
	0.06	3.870	3.870	11.73	63(1)
	0.10	3.873	3.873	11.71	33(1)

[a] Data from reference 5 except for x = 0.15.
[b] Data from reference 2.

Table II. Ranges of isomer shifts (IS), quadrupole splittings (ΔE_Q), and full width half maximum linewidths (FWHM) of subspectra observed in $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($0.05 \le z \le 0.15, 0.003 \le x \le 0.20$) synthesized by method I. Isomer shifts are relative to Fe metal at room temperature. Errors are maximum observed.

Subspectra	IS(mm/s)	ΔE_Q(mm/s)	FWHM(mm/s)
A	0.00-0.13(5)	1.89-2.09(9)	0.21-0.40(5)
B	-0.09-0.01(3)	0.87-1.13(9)	0.34-0.57(8)
C	0.27-0.39(3)	0.41-0.66(7)	0.22-0.51(8)
D	-0.11-0.08(4)	1.50-1.83(9)	0.31-0.39(7)
E	0.27(1)	0.71(6)	0.24(2)

Table III. Fitted areas of subspectra A,B,C,D and E observed in $Y_{1-z}Ca_zBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ prepared by method I for different values of x and z.

z	x	A(%)	B(%)	C(%)	D(%)	E(%)
0.00[a]	0.003		30	5	65	
	0.03	25	53	2	20	
	0.06	33	61	6		
	0.10	22	65	13		
0.05	0.003	11	29	22	38	
	0.01	35	21	31	13	
	0.06	3	42	24		
	0.10	15	34	51		
	0.15	12	41	47		
	0.20	9	44	47		
0.10	0.003	14	27	35	24	
	0.01	15	34	24	27	
	0.06	15	54	21	10	
	0.10	11	51	28	10	
	0.15	11	59	30		
	0.20	5	64	31		
0.15	0.003	43	14	16		27
	0.01	33	6	42	19	
	0.06	40	29	31		
	0.10	23	52	25		

[a] Data from reference 5.

Table IV. Lattice parameters, T_c and percentage of Fe on Cu(2) sites (%) of $Y_{0.90}Ca_{0.10}Ba_2(Cu_{1-x}Fe_x)_3O_{6+y}$ synthesized by method II.

x	a_0(Å)	b_0(Å)	c_0(Å)	T_c(K)	%
0.01	3.841	3.908	11.72	86(1)	42
0.06	3.850	3.889	11.69	61(1)	30
0.10	3.864	3.864	11.66	11(1)	37