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Changes in Fe Site Occupancy and T_c in $YBa_2(Cu_{1-x}Fe_x)_3O_y$ Through Processing

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CHANGES IN Fe SITE OCCUPANCY AND T_c IN $YBa_2(Cu_{1-x}Fe_x)_3O_y$ THROUGH PROCESSING

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Fe substitution for Cu in $YBa_2Cu_3O_y$ can give information about the local environment on the two crystallographic Cu sites through Mössbauer effect measurements. In this paper, we explore the possibility of forcing larger amounts of Fe onto the Cu (2) site which represents the CuO planes. At values near $y = 6$, the chain Cu (1) site is characteristic for Cu^+ in its linear O coordination and should preclude Fe occupation. We therefore prepared materials at elevated temperatures under N_2 where $y \sim 6$. Oxygenation to $y \sim 7$ was achieved at temperatures where metal diffusion is minimized. We used Mössbauer spectroscopy to determine the Fe site occupancy. Site preference can be expressed in terms of a distribution ratio r = MCu1/ MCu2. Creating materials with low r allows studying the effects of spatially constrained Fe on T_c, separating influences from the spatially more complex Cu (1) site.

The materials, $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ($x = 0.06$, 0.10), were prepared by the solid state reaction method. The initial, conventional (method I) treatment, consisted of sintering in air at 925 C and subsequent annealing at 850 C in flowing O_2. Portions of this conventionally treated sample were then treated according to a second method (II) involving annealing the sample in flowing N_2 at 770 C followed by annealing in flowing O_2 at 350 C.

X-ray diffraction indicates that all materials are single phase with the $YBa_2Cu_3O_y$ unit cell. Structural parameters, r and T_c for materials prepared by methods I and II are given in Table I. Conventional synthesis (method I) results in tetragonal structures, whereas method II results in orthorhombic structures. The superconducting transition onset temperatures for the sample prepared by method II are higher than for conventional Fe-doped materials.

	Method I				Method II				
x	a_0(A)	c_0(A)	r	T_c(K)	a_0(A)	b_0(A)	c_0(A)	r	T_c(K)
0.06	3.868	11.69	14.9	69(1)	3.845	3.886	11.67	2.6	81(1)
0.10	3.865	11.67	6.8	55(1)	3.850	3.882	11.67	1.9	63(1)

Table 1: Lattice constants, r and T_c for $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ($x = 0.06, 0.10$) for synthesis by methods I and II.

Room temperature Mössbauer spectra of the samples could be fit to three symmetric quadrupole-split sites. Spectra of the conventionally prepared material are similar to the literature; however, the spectra of the samples prepared by method II shows that more Fe occupies the Cu(2) site.

Partial Fe substitution for Cu in conventionally prepared $YBa_2Cu_3O_y$ leads to preferential Fe occupation on Cu(1) with O cluster formation around Fe atoms. This causes the materials to change to tetragonal for $x \sim 0.02$. However, at low values of y Fe should show an increased relative tendency to occupy the Cu(2) site where it is 5-fold oxygen coordinated (denoted (2)5) relative to the Cu(1) site where it would be lower coordinated. This is corroborated by our Mössbauer results. In particular, treatment of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ($x = 0.06, 0.10$) by Method II results in low r materials ($r = 2.6$ for $x = 0.06$) which remain orthorhombic.

The major difference in the preparation of low r material involves a relatively low temperature annealing at low O fugacity. Under these conditions, Fe on Cu(1) sites tends to scavenge for and share the minute amounts of extra O beyond $y = 6$. This leads to increased Fe clustering in low r materials. On subsequent low temperature oxygenation, larger regions of the sample remain relatively Fe poor on Cu(1) and the material stays orthorhombic. It should then also have a higher proportion of Fe in (1)5 due to extensive O sharing in the Fe clusters. Finally, we assume that the main reason for the decrease in T_c in low r materials appears to be connected with the change from tetragonal to orthorhombic structure.

Changes in Fe site Occupancy and T_c in $YBa_2(Cu_{1-x}Fe_x)_3O_y$ Through Processing

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Introduction

Fe substitution for Cu in $YBa_2Cu_3O_y$ can give useful information about the local environment on the two crystallographic Cu sites through Mossbauer effect measurements (1-6). Conventional synthesis (sintering at 950 C followed by an anneal at 400 C in air or O_2) generally results in Fe preferentially on the Cu(1) chain site, tetragonal structures (for x > 0.02) and multiple Fe-O coordinations.

In this paper, we explore the possibility of forcing larger amounts of Fe onto the Cu (2) site which represents the CuO planes. At values near y = 6, the chain Cu (1) site is characteristic for Cu^+ in its linear O coordination and should preclude Fe occupation. We therefore prepared materials at elevated temperatures under N_2 where y ~ 6. Oxygenation to y ~ 7 was achieved at temperatures where metal diffusion is minimized. We used Mossbauer spectroscopy to determine the Fe site occupancy. Site preference can be generally expressed in terms of a distribution ratio r = MCu1 / MCu2. Creating materials with low r allows studying the effects of spatially constrained Fe on T_c, separating influences from the spatially more complex Cu (1) site (O clustering).

We show that treating $YBa_2(Cu_{1-x}Fe_x)_3O_y$ (0.003 > x > 0.10) at high temperatures in inert atmospheres followed by oxygenation at low temperatures produces orthorhombic materials and increases T_c and the superconducting volume fraction. Spectroscopy of these materials show a greater percentage of Fe in the Cu(2) plane site. For example, a conventionally prepared x = 0.06 sample is tetragonal (a_o = 3.868 A, c_o = 11.69 A), T_c = 59 K, and 6.3% of the Fe is on the Cu(2) site. The sample prepared by the above method is orthorhombic (a_o = 3.845 A, b_o = 3.886 A, c_o = 11.67 A), T_c = 81 K, and 27.6% of the Fe is on the Cu(2) site. The reversal to orthorhombic structure is explained as a result of an increase of Fe in Cu(2) and of oxygen starvation-Fe clusters in the Cu(1) site (sharing O) due to synthesis involving low O fugacity at relatively low temperatures. This leaves the rest of the Cu(1) sites in an orthorhombic environment. The relatively high T_c for materials with more Fe on Cu(2) indicates that Fe on Cu(2) is not strongly detrimental to superconductivity.

Experimental

The materials, $YBa_2(Cu_{1-x}Fe_x)_3O_y$ (x = 0.06, 0.10), were prepared by the solid state reaction method described in more detail elsewhere [4]. Fe_2O_3 enriched with ^{57}Fe isotope (92.3%) was used for the x = 0.06 sample to enhance the Mossbauer effect. The initial, conventional (method I) treatment, which produces high r materials, consisted of sintering in air at 925 C for 21 h and subsequent annealing at 850 C in flowing O_2 for 2 h with slow cooling to 100 C over 10 h. Portions of this conventionally treated sample were then treated according to a second method (II) (which produces low r materials) involving subsequent annealing the sample in flowing N_2 at 770 C for 48 h and quick quenching to room temperature. This was followed by annealing in flowing O_2 at 350 C for 1 h with slow cooling to room temperature (3 h). Mossbauer spectroscopy was performed with a constant acceleration spectrometer using a ^{57}Co-Rh source. Absorbers were made by grinding the samples into a fine powder, mixing with sugar and enclosing the mixture in a plastic sample holder. Typical absorber thickness was 0.2-0.3 mg $^{57}Fe/cm^2$. Isomer shifts are reported relative to Fe metal at room temperature.

Results

X-ray diffraction indicates that all materials are single phase with the $YBa_2Cu_3O_y$ unit cell. Structural parameters, r and T_c for materials prepared by methods I and II are given in Table 1. Conventional synthesis (method I) results in tetragonal structures, whereas method II results in orthorhombic structures. Magnetic susceptibility shows the transition to superconductivity in both types of materials to be broader than with conventional undoped $YBa_2Cu_3O_7$, but no signs of phase separation appear. The superconducting transition onset temperatures for the sample prepared by method II are higher than for conventional Fe-doped materials. The superconducting volume fraction of these samples is also greater.

	Method I				Method II				
x	a_0(A)	c_0(A)	r	T_c(K)	a_0(A)	b_0(A)	c_0(A)	r	T_c(K)
0.06	3.868	11.69	14.9	69(1)	3.845	3.886	11.67	2.6	81(1)
0.10	3.865	11.67	6.8	55(1)	3.850	3.882	11.67	1.9	63(1)

Table 1: Lattice constants, r and T_c for $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ (x = 0.06, 0.10) for synthesis by methods I and II (see text).

	Method I			Method II		
Subspectra	IS (mm/s)	QS (mm/s)	%	IS (mm/s)	QS (mm/s)	%
A	-0.045(8)	1.97(1)	32.7(1)	-0.001(9)	2.07(4)	3.2(1)
B	-0.025(2)	1.06(1)	61.0(1)	-0.081(2)	1.03(9)	69.2(1)
C	0.371(5)	0.62(2)	6.3(1)	0.304(2)	0.62(1)	27.6(1)

Table 2: Isomer shifts (IS), quadrupole splittings (QS) and subspectra areas (%) for room temperature Mossbauer spectra of $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$ prepared by methods I and II (see text).

Room temperature Mossbauer spectra of $YBa_2(Cu_{0.94}Fe_{0.06})_3O_y$ could be fit to three symmetric quadrupole-split sites (A,B,C). The isomer shifts (IS), quadrupole splittings (QS) and subspectra area (%) of these 3 subspectra are summarized in Table 2. Spectra of the conventionally prepared material are similar to the literature [1]; however, the spectrum of the sample prepared by method II is different. In particular, doublets B and C increase in area at the expense of doublet A in going from method I to method II. Similar trends are observed in the spectra of the x=0.10 sample, however, small amounts of subspectra D [IS=-0.04 mm/s, QS=1.4 mm/s] are observed in the sample treated by method II. We will show elsewhere [4] in more detail that the change in the relative intensity of doublet C is due to the relatively high occupation of Fe on the Cu(2) site (low r). In particular, for this material r = 2.6, whereas r = 14.9 for the sample prepared by Method I. Changes in site occupancy have been noted before in samples with x = 0.003 and x = 0.10 [11,12]. Subspectra A and B are due to Fe substitution at the Cu(1) site in 4- and 5-fold oxygen coordination, respectively. These assignments have previously been made by us and other groups [3,4], based amongst others, on arguments involving the magnitude of QS. We note that the Mossbauer spectra do not indicate any traces of impurity phases such as Fe_2O_3 or Fe-doped CuO, $BaCuO_2$ and Y_2BaCuO_5.

During a previous study [7] it was found that conventionally prepared $YBa_2(Cu_{0.833}Fe_{0.167})_3O_7$ had an unusually low activation energy for oxygenation of 33.2 kJ compared to 88.2 kJ for x = 0. In order to demonstrate fast oxygenation kinetics we took a portion of $YBa_2(Cu_{0.9}Fe_{0.1})_3O_{6+y}$ after N_2 cooling to 300 K and annealed it in air at 300 C for several time intervals (10 minutes, 0.5 h and 1 h). While the initial material produces $T_c < 4$ K, the sample is, after only a 10-minute anneal, superconducting with an onset temperature of 75 K. Annealing for 0.5 and 1.0 h does not much further influence T_c. These results indicate that oxygen uptake is extremely fast in our samples.

Discussion

Partial Fe substitution for Cu in conventionally prepared $YBa_2Cu_3O_y$ leads to preferential Fe occupation on Cu(1) with O cluster formation around Fe atoms. This causes the materials to change to tetragonal for x ~ 0.02. However, at low values of y (low O fugacity) Fe should show an increased relative tendency to occupy the Cu(2) site where it is 5-fold oxygen coordinated (denoted (2)5) relative to the Cu(1) site where it would be lower coordinated. This is corroborated by our Mossbauer results. In particular, treatment of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ($x = 0.06, 0.10$) by Method II results in low r materials ($r = 2.6$ for $x = 0.06$) which remain orthorhombic. However, while the total Fe concentration in Cu(1) is lower in low r materials, there exists a slightly larger number of 5 fold coordinated Fe in the material prepared by method II compared to method I. This should in principle result in a trend to tetragonal structure for the low r material contrary to observation. We shall in the following offer a novel explanation for this behavior in terms of O starvation-Fe clusters in the orthorhombic material.

The major difference in the preparation of low r material involves a relatively low temperature annealing at low O fugacity. Under these conditions, Fe on Cu(1) sites tends to scavenge for and share the minute amounts of extra O beyond $y = 6$. This leads to increased Fe clustering (possibly linear) in low r materials. On subsequent low temperature oxygenation, larger regions of the sample remain relatively Fe poor on Cu(1) and the material stays orthorhombic. It should then also have a higher proportion of Fe in 1(5) due to extensive O sharing in the Fe clusters. The high percentage of Fe in (1)5 is brought out in Table 2. A schematic reprrsentation of Fe-O cluster formation in the Cu(1) plane is shown in Fig. 1. We should mention that there are no obvious signs for phase separation attendant to cluster formation either in Mossbauer or x-ray measurements.

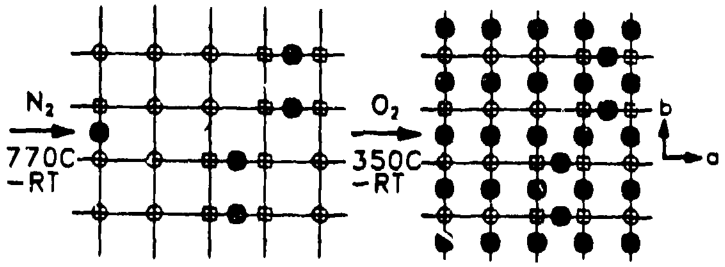

Fig. 1: Schematic representation of Fe-O cluster formation in the a-b Cu(1) plane after synthesis by method II (see text for details of synthesis). Open circles and squares represent Cu and Fe atoms, respectively. Large filled circles represent oxygen.

We assume that a main reason for the relative increase in T_c in low r materials, over conventionally prepared ones, appears to be connected with the change from tetragonal to orthorhombic structure. At the same time, however, the fraction of Fe in the Cu(2) site increases. It is now commonly assumed that the Cu(2) site is mainly responsible for superconductivity in $YBa_2Cu_3O_y$. Increased substitution in this site, therefore, should more strongly lower T_c. The relatively small reduction in T_c in low r materials compared to the unsubstituted compound indicates that Fe on Cu(2) has only a mild or perhaps no detrimental effect on superconductivity probably as it can participate to some extent in the valence fluctuations. Also, Fe atoms on Cu(1) which should localize charge and be detrimental to superconductivity are now collected in O starvation Fe clusters which are more spatially confined. These clusters should have local flux pinning properties and be of technological interest. Fe clusters with special shape and order (e.g. linear) should be achievable by annealing under low O fugacity in the range where orthorhombic structures obtain.

The present work indicates why somewhat different Mossbauer spectra can be obtained for identical x in $YBa_2(Cu_{1-x}Fe_x)_3O_y$. Variations in oxygen partial pressure, annealing temperatures and times, and cooling rates influence relative site occupancy and Fe-O coordination with low temperature annealing in O_2 or air resulting in materials with Fe primarily on the Cu(1) site in multifold O coordination.

We conclude that careful synthesis involving oxygenation at lower temperatures where Fe atoms cannot readily relocate can produce orthorhombic materials which have a greater percentage of Fe on the Cu(2) site (low r) with higher T_c than that for conventionally prepared materials. The relatively high T_c in these low r materials suggests that Fe at the Cu(2) site is not overly detrimental to superconductivity. The orthorhombic structure of low r materials is explained by an O starvation Fe cluster model, induced by the relatively low O fugacity treatment at relatively low temperatures. This concentrates Fe into special regions (with flux pinning and critical field potential) but does not influence so much the bulk of the material.

Acknowledgements

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Changes in Fe site Occupancy and T_c in $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ Through Processing

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A large body of work has been performed on the effects of partial Fe substitution for Cu in $YBa_2Cu_3O_{6+y}$ on structure, superconducting transition onset temperature T_c, Mössbauer site occupancy and magnetism [1-3]. Conventional synthesis (sintering at 950 C followed by an anneal at 400 C in air or O_2) generally results in Fe preferentially on the Cu(1) chain site, tetragonal structures (for $x \geq 0.02$) and multiple Fe-O coordinations. Synthesis techniques that affect the Fe site occupancy, structure, T_c and Fe-O coordinations would help clarify the general role of partial metal substitution for Cu in $YBa_2Cu_3O_{6+y}$ and may lead to a broader understanding in the design of high-temperature superconducting oxides.

In this paper we show that treating $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($0.003 \leq x \leq 0.15$) at high temperatures in inert atmospheres followed by oxygenation at low temperatures produces orthorhombic materials and increases T_c and the superconducting volume fraction SVF. Spectroscopy of these materials show a greater percentage of Fe in the Cu(2) plane site. For example, a conventionally prepared $x = 0.06$ sample is tetragonal ($a_0 = 3.868$ A, $c_0 = 11.69$ A), $T_c = 59$ K, SVF = 0.45 and 6.3% of the Fe is on the Cu(2) site. The sample prepared by the above method is orthorhombic ($a_0 = 3.845$ A, $b_0 = 3.886$ A, $c_0 = 11.67$ A), $T_c = 81$ K, SVF ~ 0.65 and 27.6% of the Fe is on the Cu(2) site. One can understand these facts by assuming that Fe at the Cu(2) site participates in charge fluctuations and that Fe at the Cu(1) site is surrounded by clusters of excess O which localize charge, depress T_c and form tetragonal structures.

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