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Abstract. Substitution of Fe for Cu in $Bi_2Ca_1Sr_2Cu_2O_y$ was found to be more effective in reducing T_c than in $YBa_2Cu_3O_y$. We discovered that the superconductivity which has been lost in Fe-doped $Bi_2Ca_1Sr_2Cu_2O_y$ can be greatly recovered in vacuum at about 400 °C. This suggests that the exchange interaction between the magnetic moments and superconducting pairs is not predominantly in pair-breaking mechanisms, leading to the loss of superconductivity in high-T_c ceramics.

As the non-doped and Fe-doped $Bi_2Ca_1Sr_2Cu_2O_y$ samples were subjected to vacuum annealing, the lattice parameter c was found to increase and Mössbauer data revealed that both the local structure around Fe (or Cu) sites and the relative number of Fe (or Cu) sites associated with different values of quadrupole splittings ΔQ_1 and ΔQ_2 varied. This implies that the increase in T_c for the annealed samples is related to the local distortion of Cu–O layers.

The optimum value of T_c ($\rho = 50\%$) for $Bi_2Ca_1Sr_2Cu_2O_y$ as high as 94 K can be obtained by annealing the sample in a vacuum at 500 °C for 30 min.

1. Introduction

The metallic properties of the high-T_c superconductors are generally believed to be governed by the Cu 3d and O 2p electrons. Thus magnetic impurities such as Fe, Co, Ni substituted for Cu have been made in order to understand the magnetic effect on high-T_c superconductivity [1–4]. However, in the $YBa_2Cu_3O_y$ system, there are two copper sites (i.e. the Cu(1) and Cu(2) sites associated with the Cu–O chain and the Cu–O_2 plane, respectively). For example, in Fe-doped $YBa_2Cu_3O_y$, most of the Fe atoms were found to be on Cu(1) sites [5, 6]. Unfortunately, this site has been shown by several groups [6–8] to play a less important role in high-T_c superconductivity. Therefore, although the replacement of Cu by Fe in $YBa_2Cu_3O_y$ can reduce T_c significantly, the actual role that Fe plays in high-T_c superconductors is still not understood.

In order to avoid the problems arising from two Cu sites and to understand the effects of Fe on high-T_c superconductivity better, here we study the effects of Fe on the T_c of $Bi_2Ca_1Sr_2Cu_2O_y$ in which there is only one Cu site equivalent to the Cu(2) site in $YBa_2Cu_3O_y$. We found that Fe substituted for Cu (within 3 at.% substitution) in $Bi_2Ca_1Sr_2Cu_2O_y$ reduces T_c more effectively than in $YBa_2Cu_3O_y$, but surprisingly we also discovered that the superconductivity lost in Fe-doped $Bi_2Ca_1Sr_2Cu_2O_y$ can be
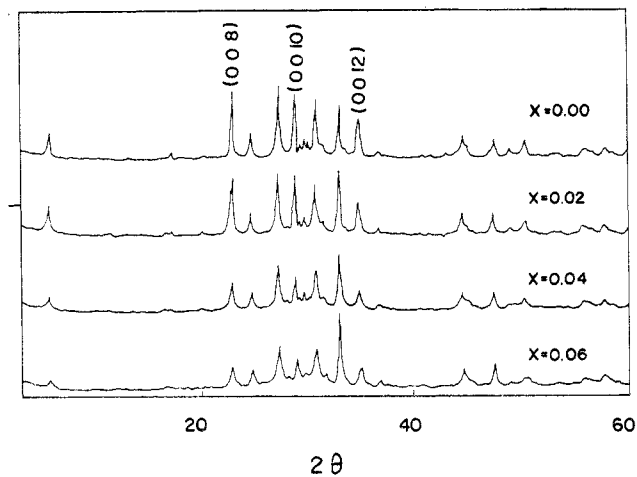
Figure 1. X-ray powder diffraction patterns for $Bi_2Ca_1Sr_2Cu_{2-x}Fe_xO_y$.

recovered by annealing the sample in a vacuum. This is in contrast to the $YBa_2Cu_3O_y$ system, in which T_c decreases when the sample is subjected to vacuum annealing.

In this work we try to elucidate how Fe and vacuum annealing affect the T_c of $Bi_2Ca_1Sr_2Cu_2O_y$.

2. Experiment

Samples were prepared with solid state reaction methods to form compounds of nominal composition $Bi_2Ca_1Sr_2Cu_{2-x}Fe_xO_y$ ($x = 0.0, 0.02, 0.04, 0.06$). 99.9% pure powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO, Al_2O_3, ZnO and Fe_2O_3 were thoroughly mixed and heated in air at 800 °C for 16 h. The reacted powder was then pulverized, pressed and sintered at 855 °C for 5 d in air and subsequently cooled in the furnace to room temperature. To study the effects of annealing temperature on the T_c of $Bi_2Ca_1Sr_2Cu_{2-x}Fe_xO_y$, the samples were annealed in a vacuum (10^{-5} Torr) at different temperatures for 30 min and T_c was determined from the plot of resistivity versus temperature T. Mössbauer spectroscopy and x-ray diffraction were employed to investigate the differences in the local structure and crystal structure between the annealed and untreated samples. For Mössbauer measurements, the Fe_2O_3 (93% enriched in ^{57}Fe) was used to make the samples. The radioactive source is ^{57}Co in a Rh matrix.

3. Results

The x-ray powder diffraction patterns for Fe-doped samples and non-doped samples are quite similar, as shown in figure 1. This suggests that their crystal structures are identical. Figure 2 displays the resistivity ρ versus temperature for $Bi_2Ca_1Sr_2Cu_{2-x}Fe_xO_y$

Figure 2. Resistivity ρ versus temperature for $Bi_2Ca_1Sr_2Cu_{2-x}Fe_xO_y$.

with $x = 0.0$, 0.02, 0.04, 0.06. The determined values of T_c (defined as $\rho = 50\%$) are 74 K, 63 K, 56 K and 52 K, respectively, for $x = 0.00$, 0.02, 0.04 and 0.06. T_c is clearly seen to drop quite rapidly with increasing x. As x is increased from 0 to $x = 0.06$ (i.e. 3 at.% substitution), T_c decreases from 74 to 52 K (it drops by 22 K). However, in $GdBa_2Cu_{3-x}Fe_xO_y$ with the same percentage of Fe substitution, T_c is reduced by only about 10 K [8]. The room-temperature (23 °C) Mössbauer spectrum of as-prepared $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ reveals that the spectrum can be well fitted by using three pairs of quadrupole doublets denoted as doublets 1, 2 and 3 as seen in figure 3. The isomer shifts δ, quadrupole splittings ΔQ, intensity ratios I and full widths $\Delta\Gamma$ at half-maximum are determined as follows: $\delta = 0.19$, 0.25 and 0.26 mm s^{-1}; $\Delta Q = 1.82$, 1.40 and 0.66 mm s^{-1}; $I = 21.7$, 51.5 and 26.8%; $\Delta\Gamma = 0.34$, 0.42 and 0.45 mm s^{-1}. Our Mössbauer results for $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ are qualitatively in agreement with those for $Bi_2Ca_1Sr_2Cu_{1.6}Fe_{0.4}O_y$ obtained by Bremert *et al* [9]. From the measurements of the isomer shifts and the quadrupole splittings, the valences of Fe cations can be identified as Fe^{4+} and Fe^{3+}. Since the crystal structure of $Bi_2Ca_1Sr_2Cu_2O_y$ has been shown to have only one Cu site with five oxygen neighbours, doublet 2 ($\Delta Q_2 = 1.40$ mm s^{-1}) can be attributed to Fe cations with a possibly distorted pyramidal coordination, but doublet 1 ($\Delta Q_1 = 1.82$ mm s^{-1}) is difficult to identify at present, since its ΔQ_1 is too large for Fe cations with five coordination. Doublet 3 with a much smaller quadrupole splitting ($\Delta Q_3 = 0.66$ mm s^{-1}) can only be attributed to Fe cations with six oxygen neighbours. This could arise because Fe cations attract one excess oxygen to form six coordination as has been observed in the Fe-doped $GdBa_2Cu_3O_y$ system [10, 11]. The facts that Fe cations have different quadrupole splittings and that the measured linewidths $\Delta\Gamma$ of the doublets are relatively broad indicates that there is a distribution in quadrupole splittings in $Bi_2Ca_1Sr_2Cu_2O_y$. This means that Cu cations are surrounded by a variety of environments and is evidence that the modulation structure exists in $Bi_2Ca_1Sr_2Cu_2O_y$ as revealed by high-resolution electron diffraction studies [12]. Similar results were also observed in Cu NQR experiments [13].

The above Mössbauer and T_c measurements seem to show that Fe substituted into a site residing on the $Cu-O_2$ plane is more deleterious to superconductivity [7, 8]. However, by annealing $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ in a vacuum (10^{-5} Torr), we found that
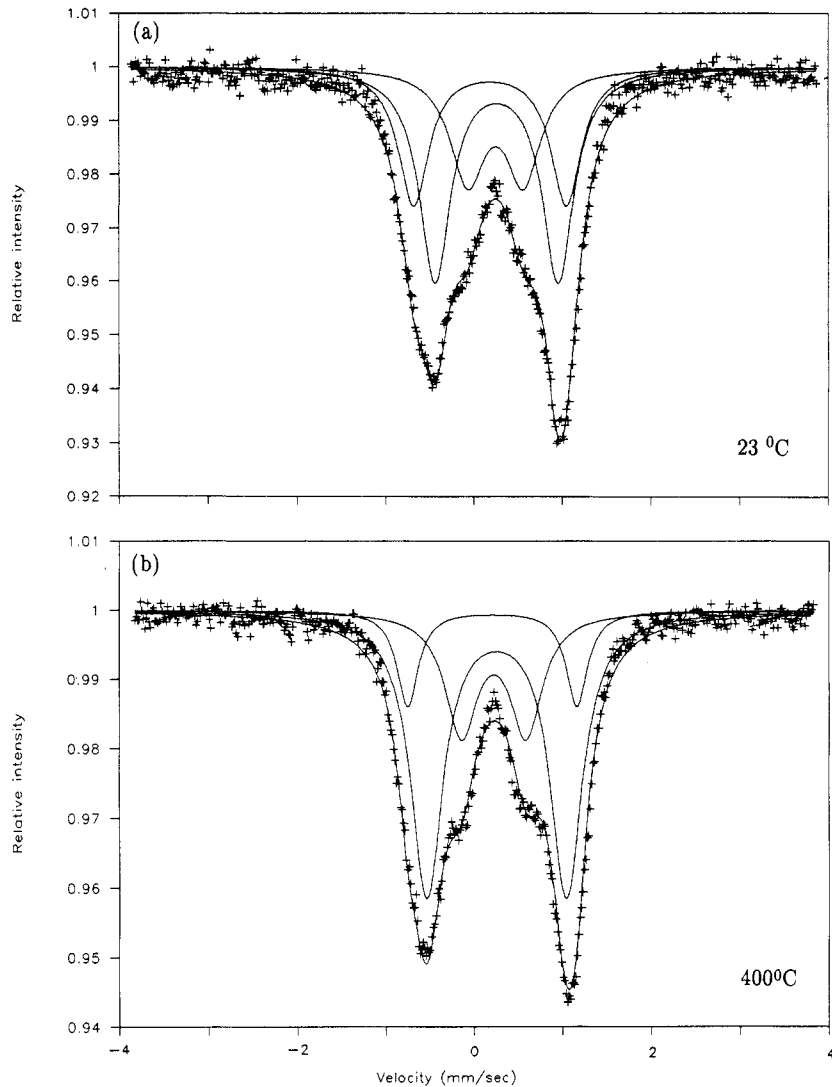
Figure 3. Room-temperature Mössbauer spectra of $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$: (*a*) untreated; (*b*) annealed at 400 °C.

the loss of superconductivity due to Fe doping could be greatly recovered. Figure 4 shows the resistivity ρ versus temperature T for $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ annealed at different temperatures: 200, 300 and 400 °C. This figure displays some interesting features.

(i) The resistivity ρ in the normal state increases with increasing annealing temperature T_a.

(ii) T_c is greatly increased as T_a is increased up to 400 °C.

For $T_a = 500$ °C, the resistivity ρ exhibits a semiconducting behaviour between 300 and 100 K and then ρ drops rapidly at about 96 K but never reaches zero, i.e. it is not a
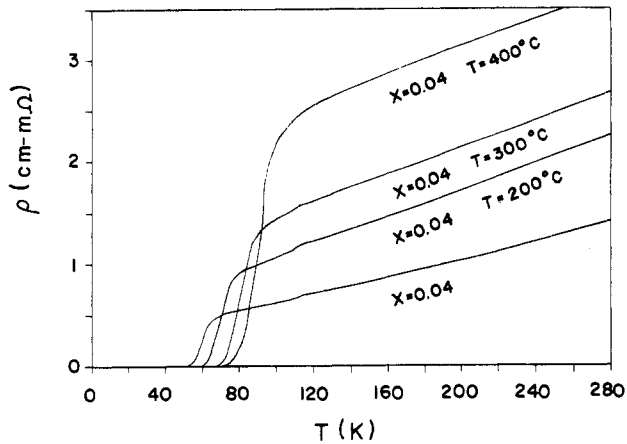
Figure 4. Resistivity ρ versus temperature T for $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ annealed at different temperatures.
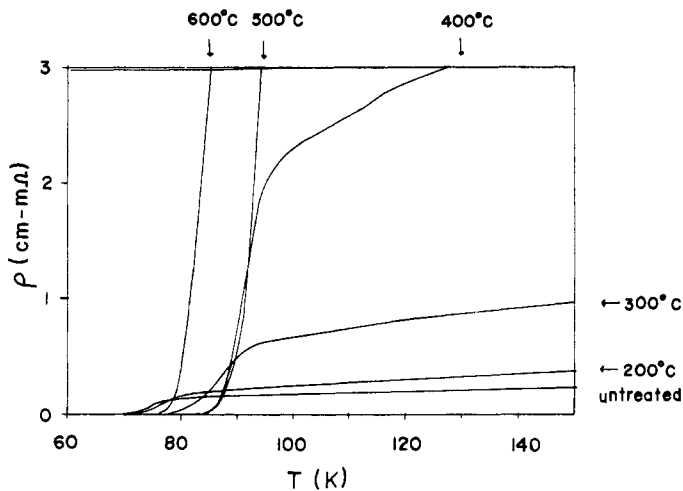
Figure 5. Resistivity ρ versus temperature T for $Bi_2Ca_1Sr_2Cu_2O_y$ annealed at 200, 300, 400, 500 and 600 °C for 30 min.

superconductor. For comparison, the resistivity ρ as a function of T for the non-doped sample $Bi_2Ca_1Sr_2Cu_2O_y$ annealed at different temperatures was also measured. The result as seen in figure 5 exhibits similar behaviour to that observed for the Fe-doped sample, i.e. both the resistivity ρ in the normal state and T_c increase with increasing annealing temperature T_a up to 500 °C. When $T_a = 600$ °C, T_c starts to decrease. The x-ray diffraction pattern shows that, at this annealing temperature, non-superconducting phases exist in the sample. T_{off} ($\rho = 10\%$), T_c ($\rho = 50\%$) and T_{on} ($\rho = 90\%$) for $Bi_2Ca_1Sr_2Cu_2O_y$ and $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ annealed at 200, 300, 400, 500 and 600 °C are listed in table 1. It is seen that, for untreated samples, T_c for $Bi_2Ca_1Sr_2Cu_2O_y$ differs from that for $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ by as much as 15 K but, after both samples have

Table 1. T_{off} ($\rho = 10\%$), T_c ($\rho = 50\%$), T_{on} ($\rho = 90\%$) for $Bi_2Ca_1Sr_2Cu_2O_y$ and $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ annealed at different temperatures T_a.

Sample	T_a (°C)	T_{off} ($\rho = 10\%$) (K)	T_c ($\rho = 50\%$) (K)	T_{on} ($\rho = 90\%$) (K)
$Bi_2Ca_1Sr_2Cu_2O_y$	Untreated	72	75	81
$Bi_2Ca_1Sr_2Cu_2O_y$	200	78	84	90
$Bi_2Ca_1Sr_2Cu_2O_y$	300	82	87	93
$Bi_2Ca_1Sr_2Cu_2O_y$	400	88	92	97
$Bi_2Ca_1Sr_2Cu_2O_y$	500	90	94	102
$Bi_2Ca_1Sr_2Cu_2O_y$	600	81	85	91
$Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$	Untreated	55	60	65
$Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$	200	64	69	75
$Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$	300	74	80	87
$Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$	400	82	90	100
$Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$	500	Non-superconductor		

Table 2. Latice parameters a, b and c for $Bi_2Ca_1Sr_2Cu_2O_y$ and $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ untreated and annealed at 400 °C.

Samples	T_a (°C)	a (Å)	b (Å)	c (Å)	Volume (Å^3)
$Bi_2Ca_1Sr_2Cu_2O_y$	Untreated	5.400 ± 0.002	5.398 ± 0.002	30.914 ± 0.003	901.118
$Bi_2Ca_1Sr_2Cu_2O_y$	400	5.409 ± 0.005	5.396 ± 0.002	31.113 ± 0.006	908.094
$Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$	Untreated	5.396 ± 0.002	5.404 ± 0.002	30.671 ± 0.002	894.365
$Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$	400	5.409 ± 0.002	5.410 ± 0.002	30.969 ± 0.003	906.236

been annealed, their T_c-values are increased by a large amount. The optimum value of T_c for $Bi_2Ca_1Sr_2Cu_2O_y$ is 94 K, while that for $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ is 90K.

The lattice parameters a, b, c determined from x-ray powder diffraction patterns for $Bi_2Ca_1Sr_2Cu_2O_y$ and $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ annealed at 400 °C and for untreated samples are compared in table 2. It can be seen that, for $Bi_2Ca_1Sr_2Cu_2O_y$, vacuum annealing does not cause a and b to vary significantly but increases c and the volume of the unit cell by about 0.64% and 0.77%, respectively, while, for $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$, it enhances c and the volume by about 0.94% and 1.33%, respectively, i.e. much more than observed for the untreated samples. The room-temperature Mössbauer spectrum of $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ annealed at 400 °C was also measured and is shown in figure 3. Table 3 shows a comparison of the determined isomer shift δ, the quadrupole splitting ΔQ, the intensity ratio I, and the full width $\Delta \Gamma$ at half-maximum for the annealed and untreated samples. It can be seen that, as the sample is annealed in a vacuum at 400 °C, the isomer shift can be regarded as unchanged within experimental error; the quadrupole splittings ΔQ_1, ΔQ_2 and ΔQ_3 are increased from 1.82 to 1.91 mm s^{-1}, from 1.40 to 1.58 mm s^{-1} and from 0.66 to 0.73 mm s^{-1}, respectively; the intensity ratio I_2 is increased

Table 3. Values of the isomer shift δ, the quadrupole splitting ΔQ, the intensity ratio I and the full width $\Delta\Gamma$ at half-maximum for $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ untreated and annealed at 400 °C.

	δ_1 (mm s^{-1})	δ_2 (mm s^{-1})	δ_3 (mm s^{-1})	ΔQ_1 (mm s^{-1})	ΔQ_2 (mm s^{-1})	ΔQ_3 (mm s^{-1})
Untreated	0.19	0.25	0.26	1.82	1.40	0.66
400 °C	0.20	0.25	0.22	1.91	1.58	0.73
	I_1 (%)	I_2 (%)	I_3 (%)	$\Delta\Gamma_1$ (mm s^{-1})	$\Delta\Gamma_2$ (mm s^{-1})	$\Delta\Gamma_3$ (mm s^{-1})
Untreated	22	51	27	0.34	0.42	0.44
400 °C	14	60	26	0.29	0.44	0.44

(from 51 to 60%) at the expense of the intensity ratio I_1 (from 22 to 14%), while the intensity ratio I_3 remains roughly constant.

4. Discussion

As was mentioned previously, the replacement of Cu by Fe in $Bi_2Ca_1Sr_2Cu_2O_y$ can reduce T_c drastically, but this cannot be attributed predominantly to the exchange interaction between magnetic spins and superconducting pairs in view of the fact that the loss of superconductivity due to Fe doping can be largely regained by annealing the sample in a vacuum. The unimportance of the exchange interaction in the pair-breaking mechanisms leading to the loss of superconductivity in high-T_c ceramics was also pointed out by Kistenmacher [14] after systematic studies of published data on the effects of substitution of transition- and non-transition-metal ions for copper in $YBa_2Cu_3O_y$.

The resistivity ρ of $Bi_2Ca_1Sr_2Cu_2O_y$ and $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ was seen to increase as the samples were subjected to vacuum annealing. This behaviour is the same as that observed in $YBa_2Cu_3O_y$ superconductors. However, in the latter system, T_c decreases with increasing resistivity rather than increases as we saw in the Bi-based system. An increase in the resistivity for annealed $YBa_2Cu_3O_y$ is attributed to both the decrease in carrier concentration and the increase in elastic scattering rate caused by the oxygen–vacancy disorder because of the loss of oxygen [15]. T_c was then found to decrease with decreasing carrier concentration [16]. However, for non-doped and Fe-doped $Bi_2Ca_1Sr_2Cu_2O_y$ subjected to vacuum annealing, we believe that the increased resistivity ρ is also related to the increased defects possibly resulting from the rearrangement of the position of oxygen and the loss of oxygen, from the evidence of the weight loss as measured by thermogravimetric analysis in an air atmosphere [17]. Although we still do not know whether or not an increase in resistivity for the annealed Bi–Ca–Sr–Cu–O systems is concomitant with a decrease in carrier concentration, Hall data [18] have indicated that in both Bi–Ca–Sr–Cu–O and Tl–Ca–Sr–Cu–O systems, T_c decreases with increase in carrier concentration n, if we equate n to the Hall number $n_H = 1/R_H e$, where R_H is the Hall constant. This suggests that the enhancement of T_c in Bi–Ca–Sr–Cu–O and Tl–Ca–Sr–Cu–O systems may not be correlated with the carrier concentration.

The lattice parameter c and the volume of the unit cell of the annealed $Bi_2Ca_1Sr_2Cu_2O_y$ and $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ have been shown to be larger than those of the untreated samples. This does not necessarily mean that the increase in T_c due to vacuum annealing is directly related to the change in crystal structure, but the change in crystal structure might indicate a change in the structure of the modulated Bi–O and Cu–O layers as revealed in the change in both the local structure around Fe (or Cu) cations and the relative number of Fe (or Cu) sites having different values of ΔQ_1 and ΔQ_2, as observed in the variation in the quadrupole splitting ΔQ and the intensity ratios I_1 and I_2. This implies that the increase in T_c for the annealed $Bi_2Ca_1Sr_2(Cu, Fe)_2O_y$ samples is related to the local distortion of Cu–O layers arising from the change in the modulation structure of Bi–O layers possibly caused by the desorption of oxygen due to vacuum annealing.

Recently both Morris *et al* [19] and Zhao and Seehra [20] have also found that T_c decreases with increasing oxygen concentration of $Bi_2Ca_1Sr_2Cu_2O_y$ by treating the sample in O_2 at an appropriate pressure (instead of vacuum annealing as we do here). They attributed it to the reduction in the Fermi level which reduces the conductivity of the Bi–O layers. However, this seems to conflict with not only the data from Hall measurements as mentioned above but also the results from scanning tunnelling spectroscopy which show that the Bi–O layers are non-metallic [21]. Therefore, the increase in T_c for the samples subjected to vacuum annealing (or the desorption of oxygen) must be due to more subtle reasons.

The following question remains: if a rapid drop in T_c in Fe-doped $Bi_2Ca_1Sr_2Cu_2O_y$ is not mainly due to Fe impurities, as mentioned above, then why does T_c for $Bi_2Ca_1Sr_2Cu_2O_y$ decrease drastically, as Cu is replaced by Fe? One possible answer to this question is that Fe-doped $Bi_2Ca_1Sr_2Cu_2O_y$ may contain more excess oxygen than non-doped samples do, because excess oxygen, as shown by us and others, is deleterious to the superconductivity in $Bi_2Ca_1Sr_2Cu_2O_y$.

To prove this, we used a thermogravimetric analyser to measure the weight loss after the sample had been annealed. Preliminary results show that the weight percentage changes, after $Bi_2Ca_1Sr_2Cu_2O_y$ and $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ had been annealed at 400 °C for 30 min, are 0.1865% and 1.0241%, respectively. This indicates that the $Bi_2Ca_1Sr_2Cu_{1.96}Fe_{0.04}O_y$ superconductor does contain much more excess oxygen.

In fact, our Mössbauer spectra indicated that extra oxygen ions are attracted to Fe cations to form octahedral coordination (which was identified as associated with doublet 3 with a quadrupole splitting $\Delta Q_3 = 0.66$ mm s^{-1} (see table 3)), but these oxygen ions seem to be tightly bound to Fe cations and are hard to release from the sample during vacuum annealing, as seen from the fact that the intensities of doublet 3 before and after annealing are almost the same. Thus the oxygen ions lost during annealing might be related to those associated with doublet 1 since its intensity decreases from 22 to 14% as the annealing temperature is increased from 23 to 400 °C. At present we are still unable to understand the origin of doublet 1 but, in view of the possibly important role that doublet 1 plays in the relationship between the location of the excess oxygen and T_c, the origin of doublet 1 deserves further investigation.

5. Conclusion

The substitution of Fe for Cu in $Bi_2Ca_1Sr_2Cu_2O_y$ has been found to reduce T_c quite rapidly. This was attributed to be mainly due to the excess oxygen introduced into the

sample by Fe doping and not to the exchange interaction between magnetic moments and superconducting pairs.

The change in the modulation structure of the Bi–O and Cu–O layers resulting from the absorption or desorption of the excess oxygen is thought to be related to lowering or raising T_c for non-doped and Fe-doped $Bi_2Ca_1Sr_2Cu_2O_y$ superconductors.

The optimum value of T_c ($\rho = 50\%$) for $Bi_2Ca_1Sr_2Cu_2O_y$ as high as 94 K can be obtained by annealing the sample in a vacuum at 500 °C for 30 min.

Further experimental and theoretical studies are needed to locate the excess oxygen exactly and to understand more quantitatively the effects of the modulation structure of Bi–O and Cu–O layers on T_c for $Bi_2Ca_1Sr_2Cu_2O_y$.

Acknowledgment

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