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Substituted $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{and Ga}$): possibility and impact of local structural disorder in CuO_2 planes

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Abstract. We report a study of metal ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{and Ga}$) substitution at Cu sites in small quantities ($x = 0.0, 0.03, 0.045$ and 0.06) in fully oxygenated ($y = 0.09$) and oxygen deficient ($y = 0.24$ and 0.32) polycrystalline $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$. In contrast to Fe, Co and Ga, the site preference (Cu–O chains/ CuO_2 planes) for Ni is found to depend on the oxygen content of the host system. The substitution of Fe, Co and Ga (and Ni in an oxygen deficient set of samples), with respect to the pure ($x = 0$) samples, results in a 10–45% reduction in orthorhombic distortion and a negligible ($y = 0.01$ – 0.03) change in oxygen content. The analysis of these variations suggests the formation of oxygen vacancy disorder in CuO_2 planes and/or in Cu–O chains, which may have an important role in determining the striking changes observed in a host of properties of $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$.

1. Introduction

There have been many studies [1–6] of metal (Fe, Co, Ni, Ga, Zn) substitution at Cu-sites in $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$ (i.e. R:123; R = rare earth) high temperature superconductors (HTSCs). It was found that trivalent cations (Fe, Co, Ga) prefer the Cu(1) site in Cu–O chains, whereas the divalent ones (Ni, Zn) prefer the Cu(2) site in CuO_2 planes. Enormous changes may result in general from these substitutions in the normal and superconducting properties of R:123. For instance, the trivalent cationic (Fe, Co and Ga) substitutions result in an orthorhombic–tetragonal (O–T) structural transition, increase in the overall oxygen content of the samples, negative temperature derivative of resistivity ($d\rho/dT$) in the normal state and suppression of superconductivity. However, despite an abundance of available literature, understanding is still limited as to how the various properties of these complex materials are affected by substitutions.

Charge transfer from the CuO_2 planes, where superconductivity seems to originate in HTSCs, to the charge reservoir layers [7, 8] has been a general approach to look for an explanation of some of these results. However, there are some clear shortcomings within such an approach. Dopants which prefer Cu(2) sites in CuO_2 planes (Ni and Zn) do not affect the charge reservoir layers at all, and for dopants occupying Cu(1) sites in Cu–O chains (Fe, Co and Ga) there is no report showing unambiguously the transfer of charge. Global measurements like thermopower and Hall constant/coefficient can indicate the overall changes in the carrier concentration [9]; however, they cannot distinguish between charge transfer and charge localization. The answer to two questions, which seem to have been overlooked so far for trivalent cationic (Fe, Co and Ga) substitutions, can be particularly instructive: (1) how

do substitutions of small amounts ($\sim 3\%$) of Fe, Co or Ga lead to an O–T transformation in the R:123 structure? (2) Since an increase in the total oxygen content would compensate any possible change in the average Cu valence resulting from these aliovalent substitutions: then what leads to a decrease in T_c especially when the substitution occurs at the Cu(1) site in Cu–O chains?

We have investigated the $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ (i.e. Er:123(M)) system with small ($x \leq 0.06$) quantities of metals ($M = \text{Fe, Co, Ni and Ga}$) substituted at Cu sites. In addition we have studied all these substitutions in the host ($x = 0$) Er:123 system with significantly different total oxygen content ($7 - y \approx 6.91, 6.76, 6.68$) to see the effects of simultaneous change in oxygen and cationic substitution. Recently [10, 11], our results for Pr and Ca substituted (at the R site) R:123 have revealed that local structural disorder in CuO_2 planes can indeed play an important role in the normal and superconducting properties. There is a weight of evidence that shows that depending on the ionic radii, degree of aliovalence and coordination number of the dopant, the R:123 structure is vulnerable to loss of oxygen from CuO_2 planes. We give evidence of similar disorder resulting in CuO_2 planes and Cu–O chains when the above trivalent cations are substituted at the Cu(1) site of Cu–O chains.

2. Experimental details

Polycrystalline samples of $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ ($M = \text{Fe, Co, Ni and Ga}$) with $x = 0.0, 0.03, 0.045$ and 0.06 were synthesized via a solid state reaction route by mixing and grinding of high purity $\text{Er}_2\text{O}_3, \text{BaCO}_3, \text{CuO}, \text{Fe}_2\text{O}_3, \text{Co}_2\text{O}_3, \text{NiO}$ and Ga_2O_3 in stoichiometric ratio. The mixed and pulverized powders were calcined at $910^\circ\text{C}, 920^\circ\text{C}$ and 930°C each for 24 hours in air with intermediate grinding for better homogeneity. Finally, all the samples were heat treated at 935°C for 24 hours, followed by an intervening step at 600°C for 12 hours and furnace cooled to room temperature in flowing oxygen. As-prepared bar shaped samples were then divided into two parts. One of the parts was subsequently annealed at 400°C for 12 hours, in flowing argon, to reduce the overall oxygen content. The argon treated piece was further divided into two parts. One of the parts was again annealed in argon at 450°C for 18 hours to further reduce the overall oxygen content.

Thus three series of samples were made for each M, namely: one with ‘full’ oxygen content (oxygenated), one with ‘reduced’ (400°C argon annealing) oxygen content and the other with ‘doubly reduced’ ($400^\circ\text{C} + 450^\circ\text{C}$ argon annealing) oxygen content. These samples will be referred to as O, A₁ and A₂ sets of samples, respectively.

X-ray diffraction (XRD) was performed to determine the unit cell parameters of all the samples of the sets O and A₂ at room temperature with the help of a D-500 Siemens diffractometer using Cu $K\alpha$ radiation. The oxygen content of all the samples of all three sets O, A₁ and A₂ was determined using a conventional iodometric technique, within a maximum error of ± 0.02 . The d.c. resistivity measurements in the temperature range 30–300 K were carried out in a closed cycle refrigerator using the standard four probe technique. The accuracy of the temperature sensor below 100 K was ± 0.5 K.

3. Experimental results

3.1. X-ray diffraction

XRD patterns of all the samples of sets O and A₂ showed the presence of only a single phase. The lattice parameters for oxygenated samples of set O are given in table 1. For the pure ($x = 0$) sample, the orthorhombic distortion (OD) and c -parameter are in good agreement

Table 1. Lattice parameters (in Å) a , b and c , orthorhombic distortion $[(b - a)/b] \times 100$, oxygen content $(7 - y)$ and average Cu valence (p^+). The lattice parameters are rounded off at the last decimal place and the maximum error in y is ± 0.02 .

Sample	a	b (Set O)	c	$[(b - a)/b] \times 100$ (Set O)	$7 - y$ (Set O)	p^+ (Set O)	$7 - y$ (Set A1)
Pure(0.0)	3.819	3.883	11.671	1.648	6.91	2.27	6.76
Fe(0.03)	3.825	3.875	11.670	1.290	6.92	2.27	6.77
Fe(0.045)	3.834	3.874	11.669	1.032	6.92	2.27	6.78
Fe(0.06)	3.833	3.872	11.650	1.007	6.93	2.27	6.80
Co(0.03)	3.821	3.879	11.670	1.495	6.92	2.27	6.77
Co(0.045)	3.829	3.877	11.691	1.238	6.93	2.28	6.77
Co(0.06)	3.824	3.874	11.687	1.291	6.93	2.27	6.78
Ni(0.03)	3.816	3.881	11.670	1.675	6.91	2.28	6.76
Ni(0.045)	3.808	3.872	11.672	1.653	6.90	2.27	6.76
Ni(0.06)	3.811	3.875	11.670	1.652	6.90	2.27	6.76
Ga(0.03)	3.820	3.870	11.670	1.292	6.92	2.27	6.76
Ga(0.045)	3.823	3.868	11.671	1.163	6.92	2.27	6.77
Ga(0.06)	3.826	3.868	11.670	1.085	6.93	2.27	6.78

with the reported data for polycrystalline R:123 [2, 4, 6]. With progressive doping of Fe, Co and Ga, we observe a reduction in the OD, see table 1. In contrast, the Ni based samples show no change in the OD, either with respect to pure Er:123 or with increase in x . These results are in complete agreement with the earlier literature [1–6]. The change in OD can also be directly appreciated by following the relative evolution of 020 and 200 reflections at $\sim 47^\circ$, and 123 and 213 reflections at $\sim 58^\circ$ in the XRD patterns. The left-hand side of figure 1 shows such an evolution for the pure, Fe and Ni substituted Er:123 samples. Co and Ga doped samples follow a behaviour similar to that of Fe. In figure 1, for the O set of samples, the relative intensity of the peaks in both the doublets change continuously with increasing Fe substitution, whereas they are invariant for Ni dopant samples. This observation supports the decrease of OD in Fe doped samples and a constant OD in Ni doped samples of the set O, and are in accord with the results shown in table 1.

The lattice parameters for the oxygen deficient samples of set A2 are given in table 2. For the pure ($x = 0$) sample, as expected [7, 12], the OD has decreased along with a corresponding increase of the parameter of the c -axis. Substitution by all four elements ($M = \text{Fe, Co, Ni}$ and Ga) leads to a further decrease in the OD with increasing x , see table 2. This feature of set A2, for Fe, Co and Ga doped samples, is similar to the one observed for set O. However, the decrease in OD for Ni doped samples of set A2, unlike the set O, indicates a possible substitution of Ni^{3+} at the Cu(1) site in Cu–O chains in oxygen deficient Er:123. Also note that (see the right-hand side of figure 1), for both Fe and Ni doped samples of set A2, the relative peak intensities in both the (020, 200) and (123, 213) doublets show a continuous change with increase in x . This feature observed in the XRD patterns endorses the change of OD in both Fe and Ni doped samples of set A2.

3.2. Iodometric titration

We show in tables 1 and 2 the iodometrically determined oxygen content in the samples for all three sets—O, A1 and A2. Consistent with the heat treatment, the pure ($x = 0$) samples

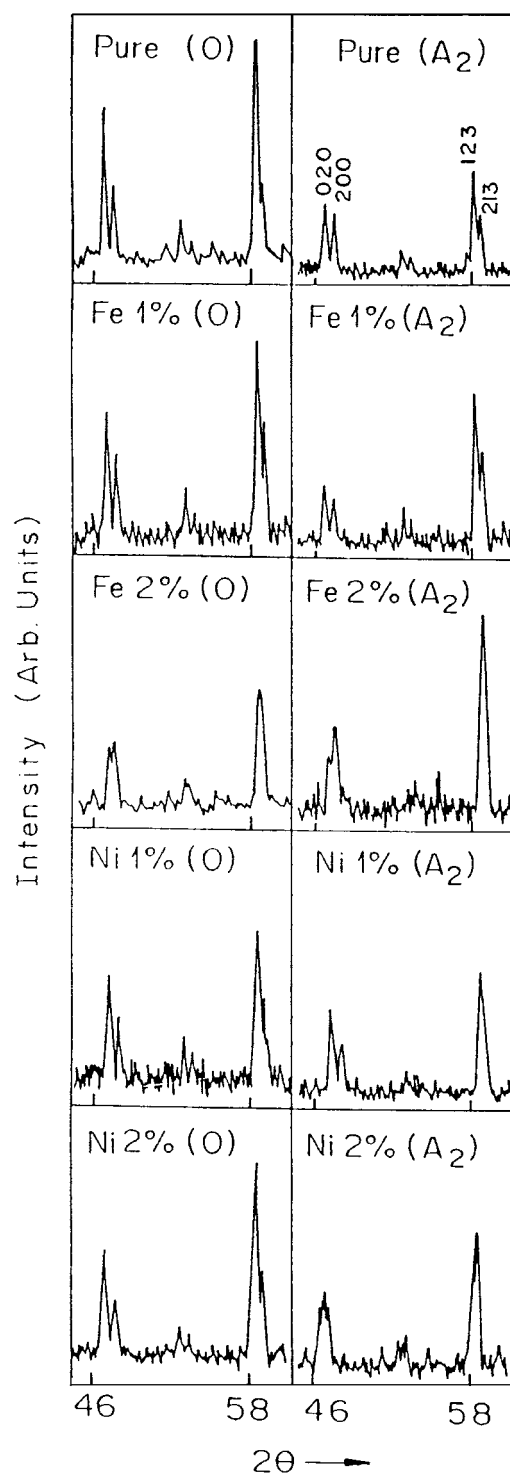


Figure 1. Evolution of the double peaks at $\sim 47^\circ$ and $\sim 58^\circ$, determined by x-ray diffraction, in pure, Fe and Ni substituted $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ samples of the sets O and A₂.

Table 2. Lattice parameters (in Å) a , b and c , orthorhombic distortion $[(b - a)/b] \times 100$, oxygen content $(7 - y)$ and average Cu valence (p^+). The lattice parameters are rounded off at the last decimal place and the maximum error in y is ± 0.02 .

Sample	a	b (Set A2)	c	$[(b - a)/b] \times 100$ (Set A2)	$7 - y$ (Set A2)	p^+ (Set A2)	p^+ (Set A1)
Pure(0.0)	3.827	3.875	11.701	1.290	6.68	2.12	2.17
Fe(0.03)	3.829	3.874	11.696	1.162	6.69	2.12	2.17
Fe(0.045)	3.830	3.874	11.691	1.136	6.69	2.11	2.17
Fe(0.06)	3.832	3.873	11.690	1.061	6.70	2.12	2.18
Co(0.03)	3.830	3.872	11.690	1.085	6.69	2.12	2.17
Co(0.045)	3.836	3.870	11.687	0.888	6.69	2.11	2.17
Co(0.06)	3.839	3.870	11.676	0.801	6.70	2.12	2.17
Ni(0.03)	3.824	3.874	11.700	1.290	6.68	2.11	2.17
Ni(0.045)	3.825	3.871	11.698	1.188	6.69	2.11	2.16
Ni(0.06)	3.827	3.872	11.690	1.162	6.70	2.12	2.16
Ga(0.03)	3.831	3.874	11.694	1.110	6.69	2.12	2.17
Ga(0.045)	3.833	3.872	11.686	1.007	6.70	2.12	2.17
Ga(0.06)	3.836	3.872	11.681	0.930	6.72	2.13	2.17

of these three sets have an overall oxygen content $7 - y = 6.91$, 6.76 and 6.68 . For all substitutions, the samples of all the three sets show only a small change in the oxygen content as compared with the pure ($x = 0$) ones. Considering the valence state of the substituting cations Fe^{3+} , Co^{3+} , Ga^{3+} and Ni^{3+} (Ni^{2+} in the samples of set O, where it occupies a Cu(2) site in the CuO_2 planes) at Cu(1) sites in Cu–O chains, the iodometrically determined oxygen content and the charge balance, we can determine the average Cu valence (p^+) in all samples. The values are given in tables 1 and 2 for all the samples. None of the substitutions leads to any appreciable change in the average Cu valence.

3.3. Normal state resistivity

Resistivity versus temperature plots for all four $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ series of samples of sets O, A1, and A2 are depicted in figures 2 to 4. For all M, the oxygenated samples of set O show a metallic $\rho(T)$ behaviour (see figure 2). For the oxygen deficient samples of set A1, the $\rho(T)$ curves start to flatten out and show a negative $d\rho/dT$ for some of the M for the highest values of x (see figure 3). The doubly oxygen deficient samples of set A2 show a rapid increase in the curvature (negative $d\rho/dT$) of the $\rho(T)$ curves with increasing x (see figure 4). The normal state $\rho(T)$ behaviour of the samples of sets A1 and A2 may be taken as a signature of their proximity to an insulating/localized state [13].

All the four series of substituted samples of set O show a break in the slope of the $\rho(T)$ curve at a characteristic temperature T^* , marked by an arrow in figure 2. The change of T^* with x for different dopants is systematic and remarkable. For $\text{M} = \text{Fe}$, Co and Ga T^* increases with x , as against a decrease observed for Ni doped samples. Pure ER:123 and Fe doped samples of the oxygen deficient set A1 show an increase in T^* (see figure 3). However, in the Ni, Co and Ga based samples of set A1, and all the M based samples of set A2, the present of T^* is not easily discernible. This may be due to the fact that T^* for these samples has shifted to $T > 250$ K, beyond the range of our measurements.

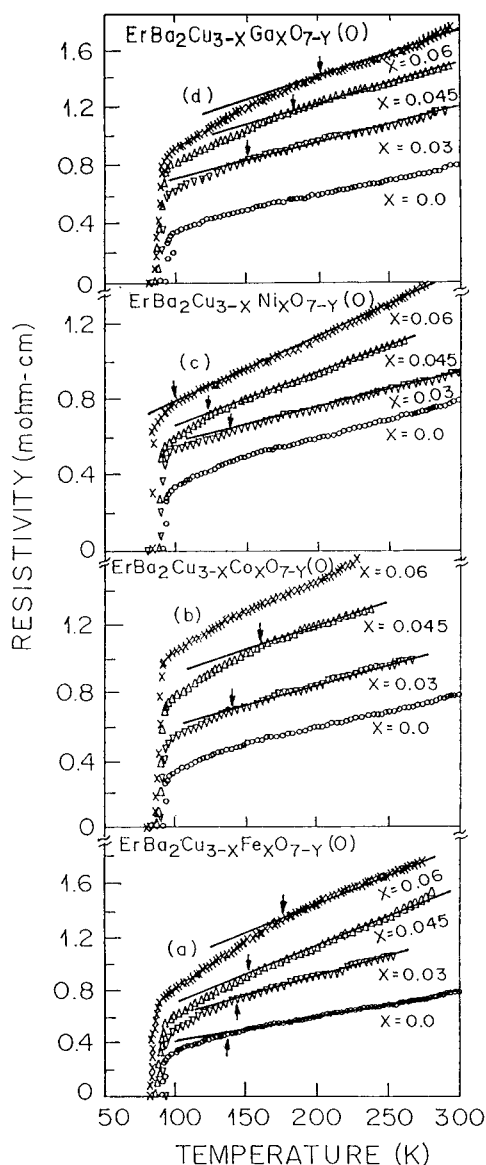


Figure 2. Resistivity as a function of temperature for the Fe, Co, Ni and Ga substituted $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ series of set O. The arrows indicate the position of T^* .

3.4. Change of T_c with x and y

As noted in figures 2 to 4, $T_c(\rho = 0)$ decreases with increasing x for all M and different y . Figure 5 shows the T_c values as a function of y and for different values of x for all the samples of series $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$. For all M, and for all the values of x , we observe a characteristic curvature in T_c with increasing y . It is well known [7, 8] for pure Er:123, that with decreasing oxygen content the $T_c(y)$ shows a curvature before reaching a plateau at around 60 K. In our samples the observed curvature in $T_c(y)$ (see figure 5) may have a similar origin.

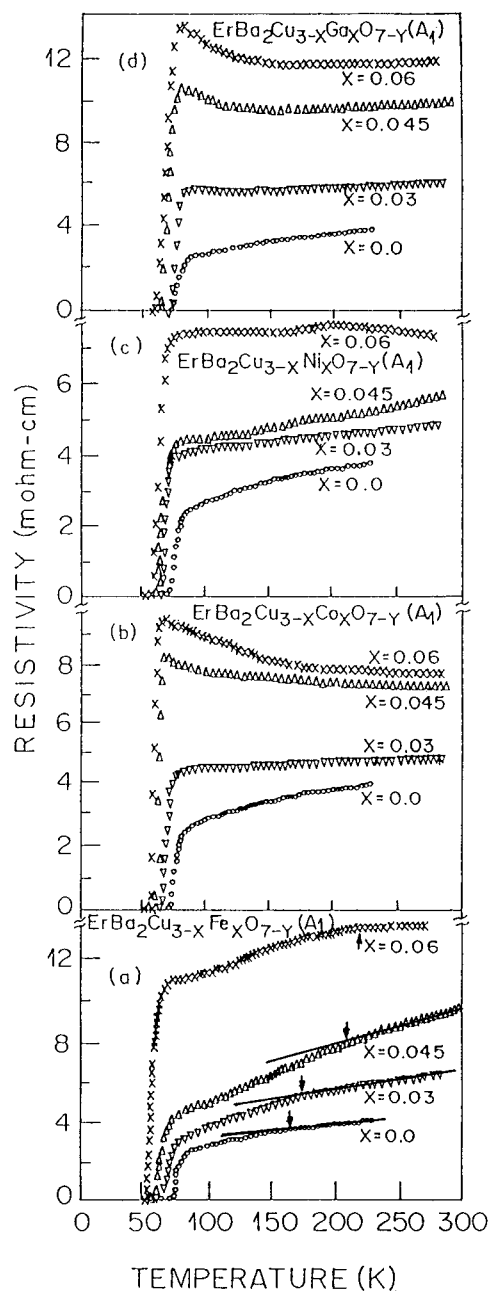


Figure 3. Resistivity as a function of temperature for the Fe, Co, Ni and Ga substituted $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ series of set A1.

We also note from figure 5 that the $T_c(y)$ curves shift to lower temperatures with increasing value for x for all dopants. In addition, by looking along the vertical lines cutting the three $T_c(y)$ curves in figure 5, for any of the dopants, one may notice that the rate of suppression of T_c with x depends on the value of y . To see this effect more carefully, we plot in figure 6 T_c as

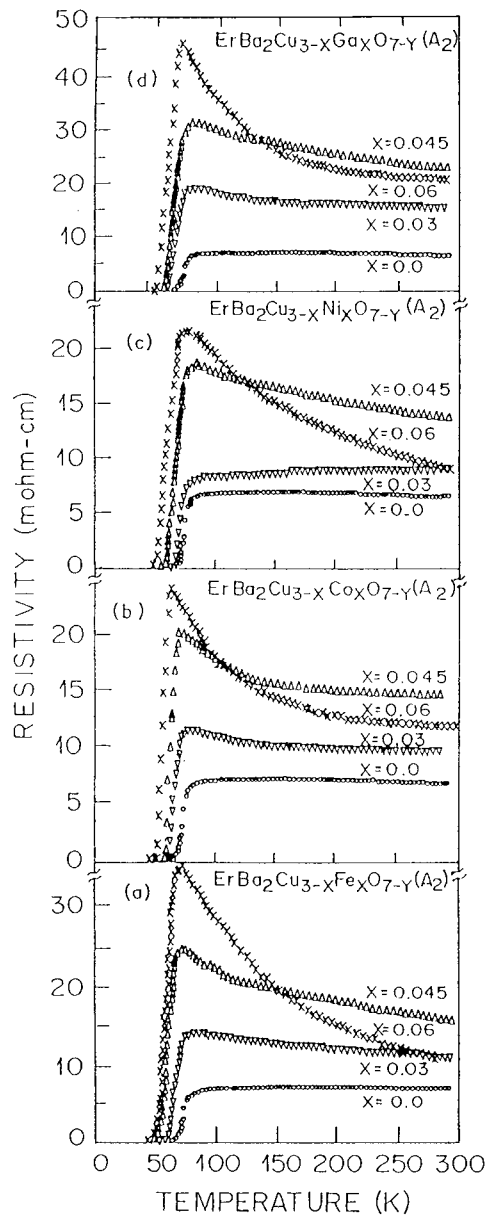


Figure 4. Resistivity as a function of temperature for the Fe, Co, Ni and Ga substituted $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ series of set A2.

a function of x for different values of y for all the series of samples. We note immediately that the slope of $T_c(x)$ increases with y for all the dopants. The slope jumps to much higher values for oxygen deficient samples of sets A1 and A2 when compared with those of the oxygenated set O. Any other definition of T_c (e.g. $0.5\rho_n$) does not change the $T_c(x)$ slopes significantly.

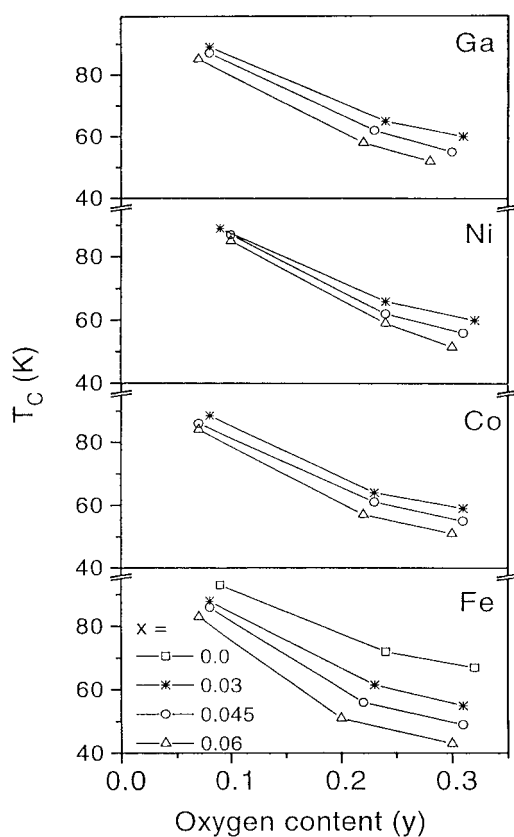


Figure 5. $T_c(\rho = 0)$ versus oxygen content (y), at different constant dopant concentration (x), for the Fe, Co, Ni and Ga substituted $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ series. The maximum measurement error in T_c is ± 0.5 K and in y is ± 0.02 .

4. Discussion

We will start our discussion by showing that the XRD and iodometry results taken together indicate oxygen vacancy disorder in Er:123(M). With the help of these results, we shall try to establish a correlation between the normal state resistivity and $T_c(x, y)$. Next, in brief, we consider a possible correlation between $T^*(x)$ and $T_c(x)$. Finally we argue that the experimental results obtained in the present work are not a consequence of the microstructure related factors in the samples.

4.1. Indications of oxygen vacancy disorder

For metal substitutions at Cu(1) chain sites in Er:123 the decrease in OD can occur owing to the O(5) chain sites (adjacent to the dopant) becoming partially filled and its occupancy coming closer to O(1) chain sites. One obvious reason for this could be a preference of a sixfold oxygen coordinated environment by Fe, Co and Ga, where their respective ionic radii 0.55 Å, 0.53 Å and 0.62 Å are ideal for substituting the Cu(1) site in Cu–O chains with 0.65 Å as ionic radius. The filling of the O(5) sites should lead to an increase in the total oxygen

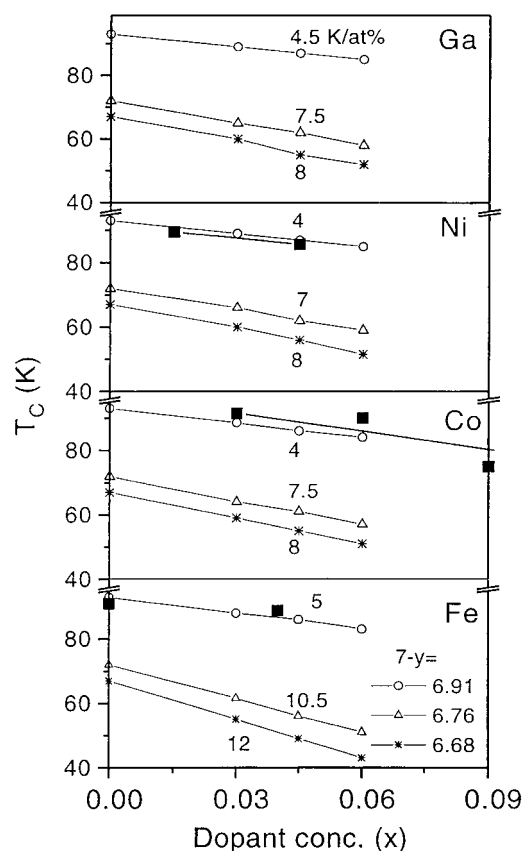


Figure 6. $T_c(\rho = 0)$ versus dopant concentration (x), at different constant oxygen content (y), for the Fe, Co, Ni and Ga substituted $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ series. The maximum measurement error in T_c is ± 0.5 K. Also included in the figure are the data (shown by solid symbols) of Fe [18], Co [19] and Ni [20] doped single crystals of R:123 ($y \approx 0$).

content of the substituted samples. Considering that the Cu(1) site has an occupancy of $1/8$ and the O(5) site has an occupancy of $1/4$, and that we require to fill two O(5) sites to provide sixfold coordination, each doped Fe atom will require an addition of four oxygen atoms. Note that this argument holds only for small amounts of M and for random substitution in the grains. However, in our Fe, Co and Ga (and oxygen deficient set of Ni) doped samples the decrease of OD is not accompanied by any significant change in the total oxygen content (e.g. for $x = 0.03$, y should have increase by 0.12: compare this with the maximum change observed in $y \approx 0.02$ shown in table 1). The only way these facts can be reconciled is if the required oxygen is transferred from either CuO_2 planes and/or from the filled O(1) sites (next to the Cu(1)) to the empty O(5) sites (next to the dopants). Such a transfer would indeed create oxygen vacancy disorder in the CuO_2 planes and/or Cu–O chains of the Fe, Co and Ga doped Er:123 samples. Also note that for oxygen deficient sets A1 and A2, in comparison to set O, a larger number of oxygen vacancies would be required to satisfy the sixfold coordination of doped trivalent M.

4.2. Correlation between T_c and ρ

For all M, we find that a decrease in $T_c(x)$ generally correlates with the normal state resistivity behaviour. For instance, for samples of set O, the residual resistivity obtained by an extrapolation of the linear part of the $\rho(T)$ plot (in figure 2) increases with increasing x for all M. Simultaneously, $T_c(x)$ is found to decrease with an increase in x for all M. For samples of sets A1 and A2, all substitutions show a stronger impact on normal state resistivity behaviour, where Er:123(M) is seen to approach an insulating/localized state (see figures 3 and 4). Indeed, for sets A1 and A2, we see that the rate of T_c depression with x also increases (see figure 6). This shows that T_c correlates with normal state resistivity. Such a correlation can be appreciated, if the suggested oxygen vacancies (the Ni sites) in Fe, Co and Ga doped (Ni doped) samples of set O are held responsible for the increase in residual resistivity. For samples of sets A1 and A2, for all M, the stronger impact of substitution on $\rho(T)$ also seems consistent with the increase in the number of oxygen vacancies in oxygen deficient Er:123(M).

It may also be inferred that, had these vacancies been created mainly in the Cu–O chains (at O(1) site next to Cu(1)), $T_c(x)$ for all sets of samples should have shown a curvature similar to the pure R:123 system (the ‘60 K plateau’ [7, 8], see also figure 5). However, for all sets of samples, a linear change observed in $T_c(x)$ (see figure 6) suggests that the oxygen vacancies are mainly created in the CuO_2 planes.

4.3. Correlation between T^* and T_c

A break in the slope of the $\rho(T)$ plot at T^* in pure R:123 has been attributed to the opening of a pseudogap [14, 15]. The observed decrease of $\rho(T)$ at T^* may reflect a decrease in scattering by magnetic fluctuations [14]. However, the origin of the pseudogap may also be related to striped phase formation or preformed pairs which in the presence of phase fluctuations form a Bose condensate only at $T_c < T^*$ [16]. Our results show that doping of Fe, Co and Ga in the oxygenated Er:123 system enhances T^* (see figure 2), or in other words enhances the magnetic fluctuations/the striped phase formation/the preformed pairs. In contrast Ni substitution suppresses T^* (see figure 2), or in other words suppresses the magnetic fluctuations/the striped phase formation/the preformed pairs. However, the fact that $T_c(x)$ is suppressed in both the cases obviously suggests that T^* is not directly correlated with T_c in a simple way. To be conclusive, more work is required by either using other powerful techniques like NMR, neutron scattering, APRES etc, to determine $T^*(x)$ in doped Er:123(M); or extending the transport measurements to samples with higher x and $T > 300$ °C.

4.4. Possible effects of various microstructural factors

One of the main purposes of the present work was to study the normal and superconducting properties of the Fe, Co, Ni and Ga doped Er:123(M) polycrystalline system. The resistivity of polycrystalline samples will be mainly determined by the transport along well connected (a, b)-planes across the grain boundaries. This follows from the anisotropic resistivity of the R:123 compounds, which is ≈ 20 times smaller along the (a, b)-planes than along the c -axis (across the CuO_2 planes) [17]. Note also that the anisotropy further increases with decreasing oxygen content [17], i.e. in samples of sets A1 and A2, the electrical transport will be along (a, b)-planes for all practical purposes. Thus it becomes imperative to ensure that the observed changes in the electrical transport properties are not caused by an extrinsic microstructure related changes introduced by doping. The possible factors due to doping, which can affect

the results extrinsically, can chiefly be texturing, inhomogeneity and segregation of the dopants at grain boundaries. Before we discuss them, we mention that the chosen range of concentration in the present work, *viz.* $0 \leq x \leq 0.06$, for all the dopants ($M = \text{Fe, Co, Ni}$ and Ga) in $\text{ErBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ is much smaller than the typical solubility regimes reported for them [1–6].

The fact that, with a change in x and y , we did not observe any anomalous enhancement of the $00l$ peaks in the XRD patterns rules out the possibility of texturing with increased dopant addition. The second factor of inhomogeneity at the grain boundaries would result in a T_c distribution that could have manifested itself in the $\rho(T)$ behaviour near the superconducting onset and when ρ goes to zero. None of the samples, as depicted in figures 2 to 4, show any broadening near superconducting onset and/or a tail at temperatures where ρ goes to zero. If the dopants had segregated at the grain boundaries, it should have resulted in no systematic change in $T_c(x, y)$ and $\rho(T, x, y)$ behaviour, which is contrary to the observations. Also, a good agreement (see figure 6) between the rate of T_c depression with x for our doped polycrystalline samples and similar data reported [18–20] for single crystals negates the possibility of inhomogeneity or segregation of dopants at grain boundaries.

Considering these observations and the fact that all our samples are prepared under identical synthesis conditions, we feel that the present analysis of various dopants with respect to the pure sample is justified as a first approximation. Finally, in HTSC doped with impurities, we believe that the microstructure may not be strongly correlated with the suppression of superconductivity. An important evidence of that is the observation of similar rates of T_c depression with increased dopant concentration, in both single crystals and polycrystalline materials. Secondly, there are models [21] which explain the behaviour of HTSCs on the basis of quantum percolation, which need disorder at the nanoscale, and make the microstructural details redundant as far as the mechanism of superconductivity is concerned.

5. Conclusions

We showed that the enormous changes found in the properties of the Er:123 system induced by very small quantities ($\leq 2\%$) of trivalent Fe, Co and Ga cationic substitution at Cu(1) sites in Cu–O chains—like the increase in ρ and rapid appearance of negative $d\rho/dT$, T_c suppression (8–24 K)—can be related to the decrease in orthorhombic distortion (10–45%) and small changes ($y = 0.01$ – 0.03) in the total oxygen content of the samples. The change in the overall oxygen content with these substitutions seems to occur only to preserve the average Cu valence, which shows no appreciable change with respect to the host compound. We propose that substitution of trivalent M cations preferring sixfold oxygen coordination at the Cu(1) site in Cu–O chains might result in removal of oxygen from CuO_2 planes and/or Cu–O chains (O(1) sites next to Cu(1)) creating oxygen vacancy disorder. Such a disorder can account for the observed correlation between resistivity behaviour and suppression of T_c with increasing substitution.

In oxygenated Er:123 samples with divalent Ni substitution, it is the Ni-site disorder in CuO_2 planes which replaces the oxygen vacancy disorder suggested in the cases of Fe, Co and Ga. However, in the oxygen deficient Er:123, the Ni substituted samples show results similar to those of Fe, Co and Ga, suggesting substitution of trivalent Ni at the Cu(1) site in Cu–O chains.

In oxygenated Er:123(M) T^* is found to decrease with Ni doping, whereas it increases for Fe, Co and Ga doping. However, more work is required to establish a correlation between T^* and T_c in these systems.

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