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EFFECTS OF SUBSTITUTION FOR CU IN $YBa_2Cu_3O_{7-d}$ AND $YBa_2Cu_4O_8$

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ABSTRACT

Structural and superconducting effects of substitution for Cu in $YBa_2Cu_3O_{7-d}$ and $YBa_2Cu_4O_8$ high T_c superconductors have been investigated. A structural change has been observed for Fe,Co,Al and Ga substitutions in $YBa_2Cu_3O_{7-d}$ and for Fe substitution in $YBa_2Cu_4O_8$. It was found that all substitutions in $YBa_2Cu_3O_{7-d}$ and $YBa_2Cu_4O_8$ reduce T_c with very different rates.

$YBa_2Cu_3O_{7-d}$ VE $YBa_2Cu_4O_8$'DE BAKIRA KATKI YAPMANIN ETKİLERİ

ÖZET

Yüksek T_c'li $YBa_2Cu_3O_{7-d}$ ve $YBa_2Cu_4O_8$ süperiletkenlerde bakıra katkı yapmanın yapıya ve süperiletkenliğe etkileri incelendi. $YBa_2Cu_3O_{7-d}$ 'de Fe,Co,Al and Ga katkıları için ve $YBa_2Cu_4O_8$' de Fe katkısı için yapısal bir değişme gözlendi. $YBa_2Cu_3O_{7-d}$ ve $YBa_2Cu_4O_8$'de bütün katkı maddelerinin T_c yi çok farklı oranlarda düşürdükleri bulundu.

1. INTRODUCTION

The discovery of $YBa_2Cu_3O_{7-d}$ high T_c superconductor [1] was significant because its T_c (92K) is higher than the boiling point of nitrogen (77K). For d<0.6, it has an orthorhombic structure. In this system Cu has two sites: namely; Cu(1) chain site (CuO) and Cu(2) plane site (CuO_2) with one Cu(1) and two Cu(2) sites in the unit cell. The oxygen stoichiometry is not stable, thus d in $YBa_2Cu_3O_{7-d}$ can take any value between 0 and 1. As a result of this, the structure and superconductivity are sensitive to the oxygen stoichiometry.

The first evidence for the existence of $YBa_2Cu_4O_8$ came from the electron microscopy study of lattice defects in $YBa_2Cu_3O_{7-d}$[2]. Later it was prepared as a bulk superconductor by several research groups using a high oxygen pressure [3,4] and finally under one atmosphere air pressure [5]. $YBa_2Cu_4O_8$ has a T_c of 80K. The crystal structure of this compound is closely related to $YBa_2Cu_3O_{7-d}$ having an additional CuO chain. The existence of additional CuO chains results in a much longer c lattice parameter and a stable oxygen content.

Substitution studies for Cu in $YBa_2Cu_3O_{7-d}$ and $YBa_2Cu_4O_8$ are of interest from both the structural and superconducting point of view. Since $YBa_2Cu_3O_{7-d}$ and $YBa_2Cu_4O_8$ have two copper sites, the contrasting effects of substitution for Cu in these two sites of these superconductors are of considerable interest. It is widely believed that superconductivity in these superconductors occurs at CuO_2 planes. Therefore it is important to determine the role of the chains and the planes in the superconductivity of $YBa_2Cu_3O_{7-d}$ and $YBa_2Cu_4O_8$.

In this study, structural and superconducting properties of Cu site substituted $YBa_2Cu_3O_{7-d}$ and $YBa_2Cu_4O_8$ have been investigated.

2. EXPERIMENTAL

The superconducting $YBa_2(Cu_{1-x}M_x)_3O_7$ (M=V, Fe, Co, Ni, Zn, Al and Ga) samples were prepared by the solid state reaction method [6]. $YBa_2(Cu_{1-y}M_y)_4O_8$ (M=Fe and Zn) samples were prepared at one atmosphere oxygen pressure using two step process first developed by Cava et. al. [5].

X-Ray Diffraction (XRD) measurements of the fully oxygenated samples were carried out at room temperature. A typical XRD powder pattern of orthorhombic $YBa_2Cu_3O_{7-d}$ is given in Fig.1. The (200), (020) and (006) peaks correspond to the lattice parameters a, b and c, respectively. XRD Powder pattern for $YBa_2Cu_4O_8$ is presented in Fig.2. The (200), (020) and (00$\underline{14}$) peaks in $YBa_2Cu_4O_8$ correspond to the (200), (020) and (006) peaks in the powder pattern of $YBa_2Cu_3O_{7-d}$. For each substitution, the T_c values were determined from A.C. susceptibility measurements.

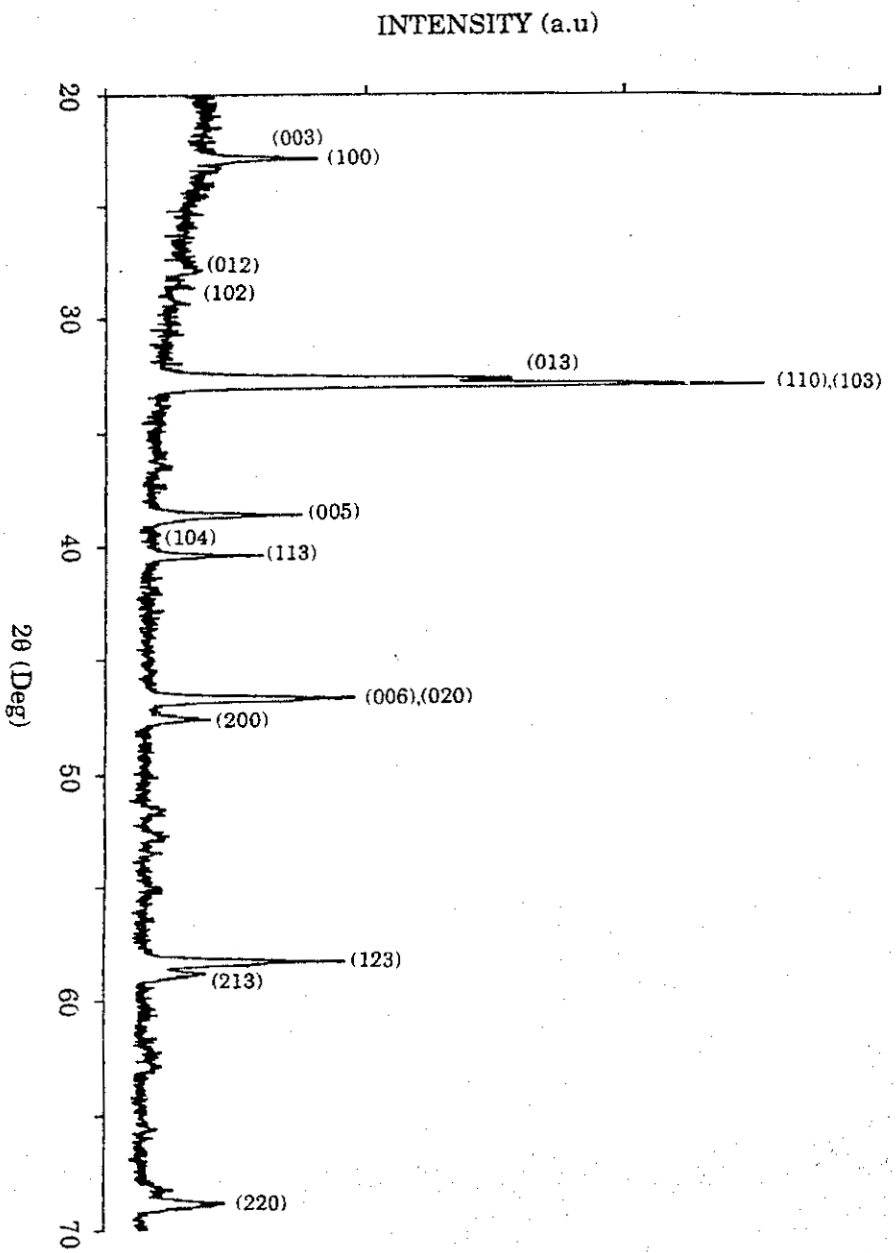
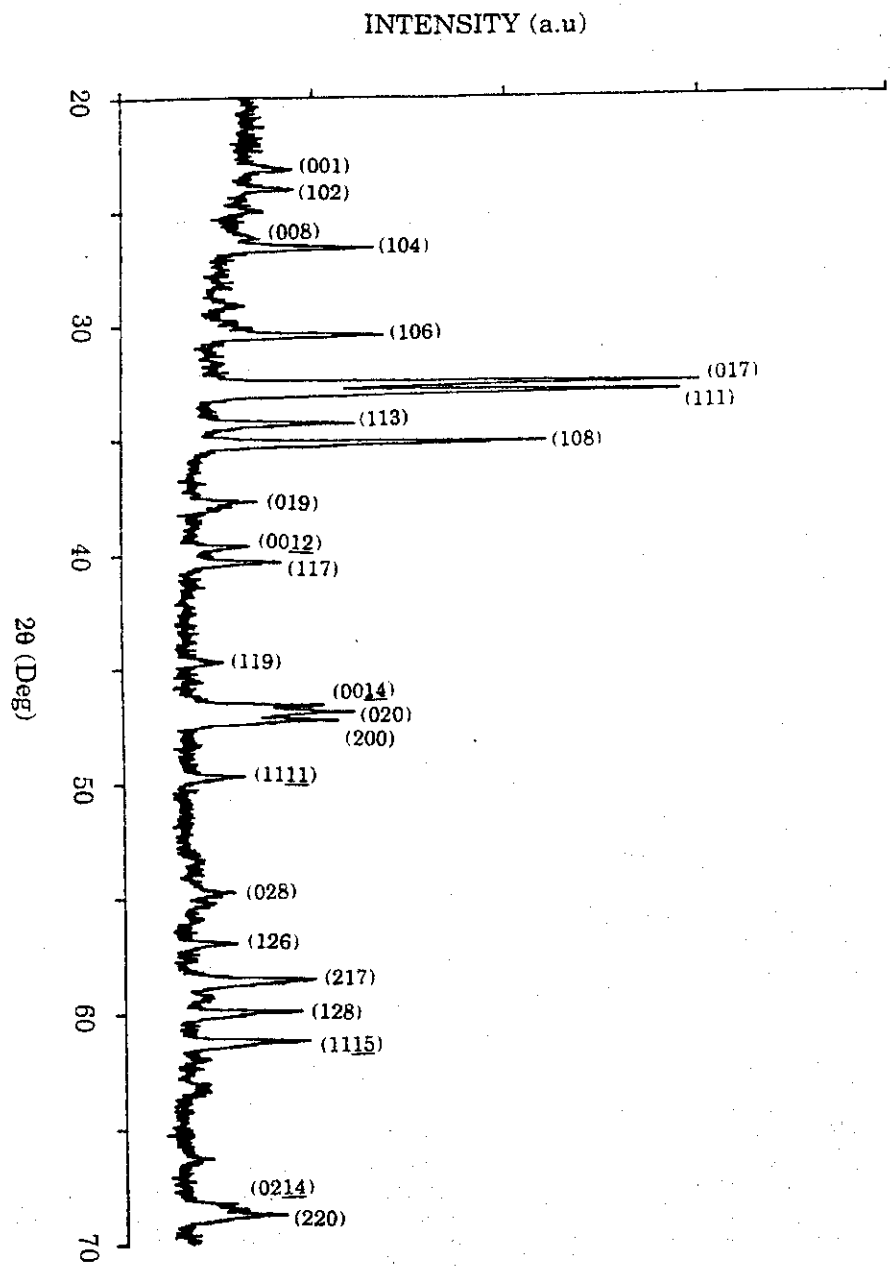


Figure 1. XRD Powder Pattern of Orthorhombic $YBa_2Cu_3O_{7-d}$ at Room Temperature.



Fligure 2. XRD Powder Pattern of $YBa_2Cu_4O_8$ at Room Temperature.

3. RESULTS AND DISCUSSION

XRD measurements have been carried out to identify the crystal structure of substituted $YBa_2(Cu_{1-x}M_x)_3O_{7-d}$ (M=V, Fe, Co, Ni, Zn, Ga and Al) and $YBa_2(Cu_{1-y}M_y)_4O_8$ (M=Fe and Zn) samples. For undoped $YBa_2Cu_3O_{7-d}$, the lattice parameters calculated from the (200), (020) and (006) peaks are a=3.827Å, b=3.882Å and c=11.682Å. The splitting of the (200) and (020) peaks in the XRD patterns of $YBa_2Cu_3O_{7-d}$ and $YBa_2Cu_4O_8$ systems simply indicate that the structure is orthorhombic. It has been observed that, for some of the substitutions (Fe, Co, Ga and Al), XRD powder patterns present a tetragonal structure for x>0.025. XRD powder patterns of $YBa_2(Cu_{1-x}Co_x)_3O_{7-d}$ for 2q=45-50 are displayed in Fig.3 as an example. The splitting of the (200) and (020) peaks disappears for x>0.025 as the structure becomes tetragonal. Also XRD powder patterns of $YBa_2(Cu_{1-x}M_x)_3O_{7-d}$ (where M=Cu, V, Ni, Zn, Fe, Co, Ga and Al; and x=0.1) are presented in Fig.4 for 2q=45-50. Again the nonexistence of the splitting of the (020) and (200) peaks shows that the structure is tetragonal for Fe, Co, Ga and Al substitution. For other substitutions (V, Ni and Zn) the structure remains orthorhombic. There have been many structural studies in substituted $YBa_2(Cu_{1-x}M_x)_3O_{7-d}$ [e.g.7-10]. Our XRD results are in good agreement with these studies. A ^{89}Y NMR study giving a clear evidence for the structural change was also reported elsewhere [11].

As known, $YBa_2Cu_4O_8$ has an orthorhombic structure. The lattice parameters of $YBa_2(Cu_{1-y}M_y)_4O_8$ obtained from the XRD powder patterns are plotted in Fig.5(a) and (b) for Zn and Fe substitution, respectively. As seen from Fig.5(a), for Zn doped $YBa_2Cu_4O_8$ samples, the crystal structure remains orthorhombic with only very small changes in the lattice parameters. For Fe substitution (Fig.5(b)), a and b lattice parameters move closer as the dopant concentration increases. By 3% substitution of Fe, a and b are almost equal and the structure is close to being tetragonal. It is clear that the structure will be entirely tetragonal by 5% Fe substitution. These results are in

good agreement with a paper by Felner and Brosh which states that the structure becomes tetragonal by 5% Fe substitution [12].

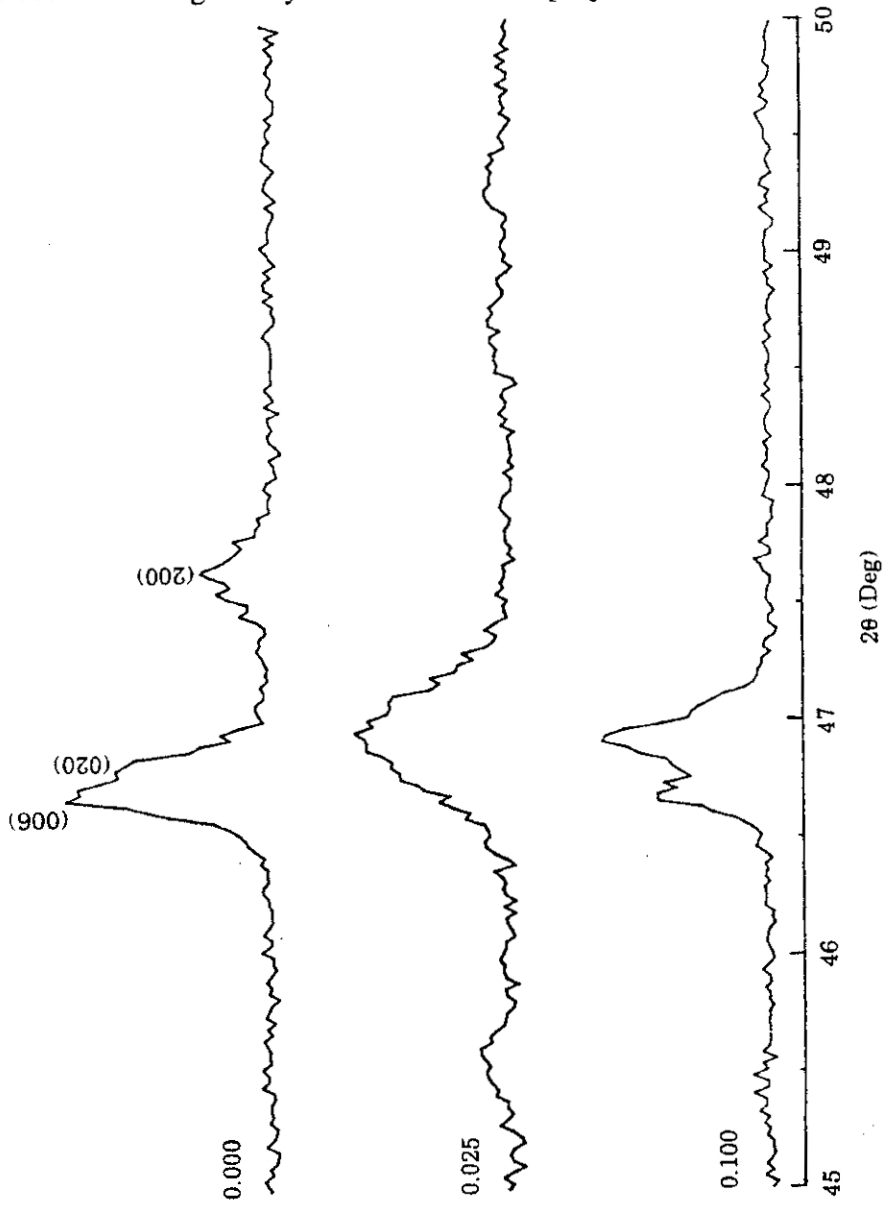


Figure 3. XRD Powder Patterns for $YBa_2(Cu_{1-x}Co_x)_3O_7$ with x=0-0.1 and 2q=45-50.

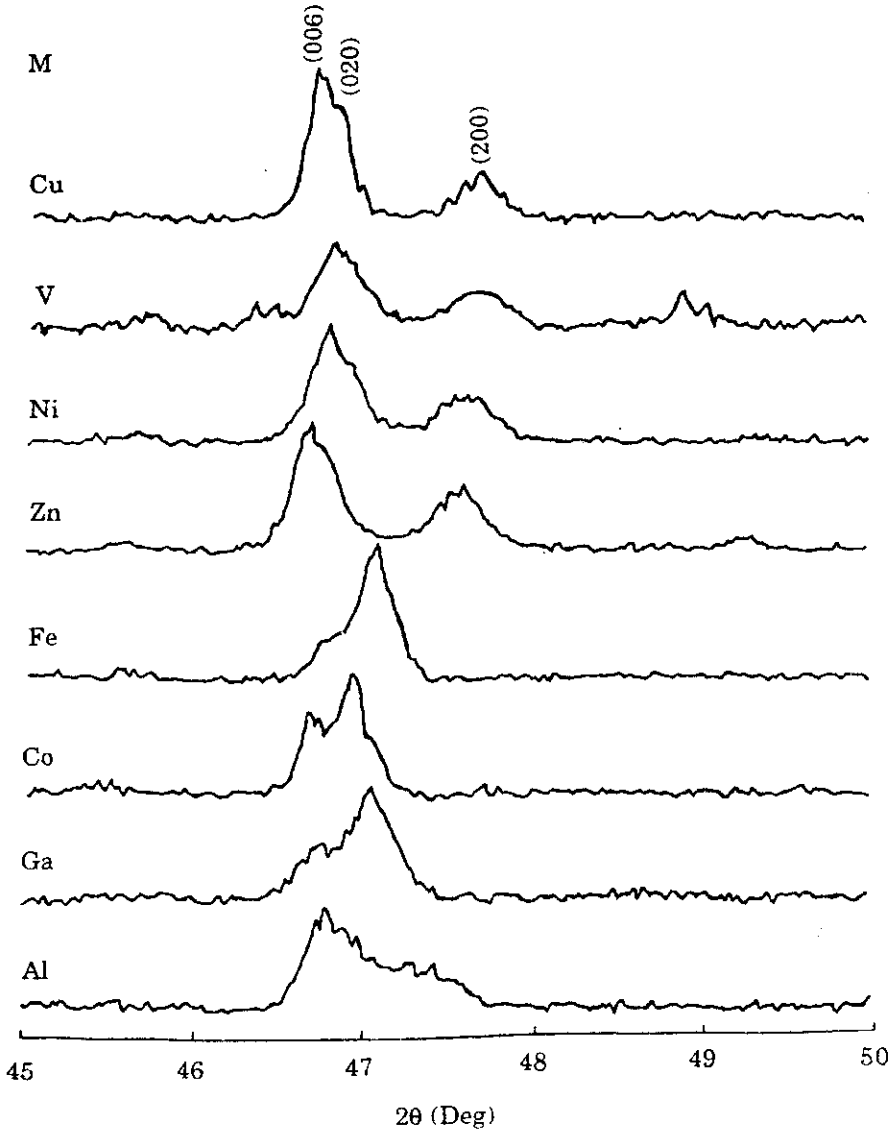


Figure 4. XRD powder patterns for $YBa_2(Cu_{1-x}M_x)_3O_7$ with 2q=45-50. Where x=0.1 and M=Cu, V, Ni, Zn, Fe, Co, Ga and Al.

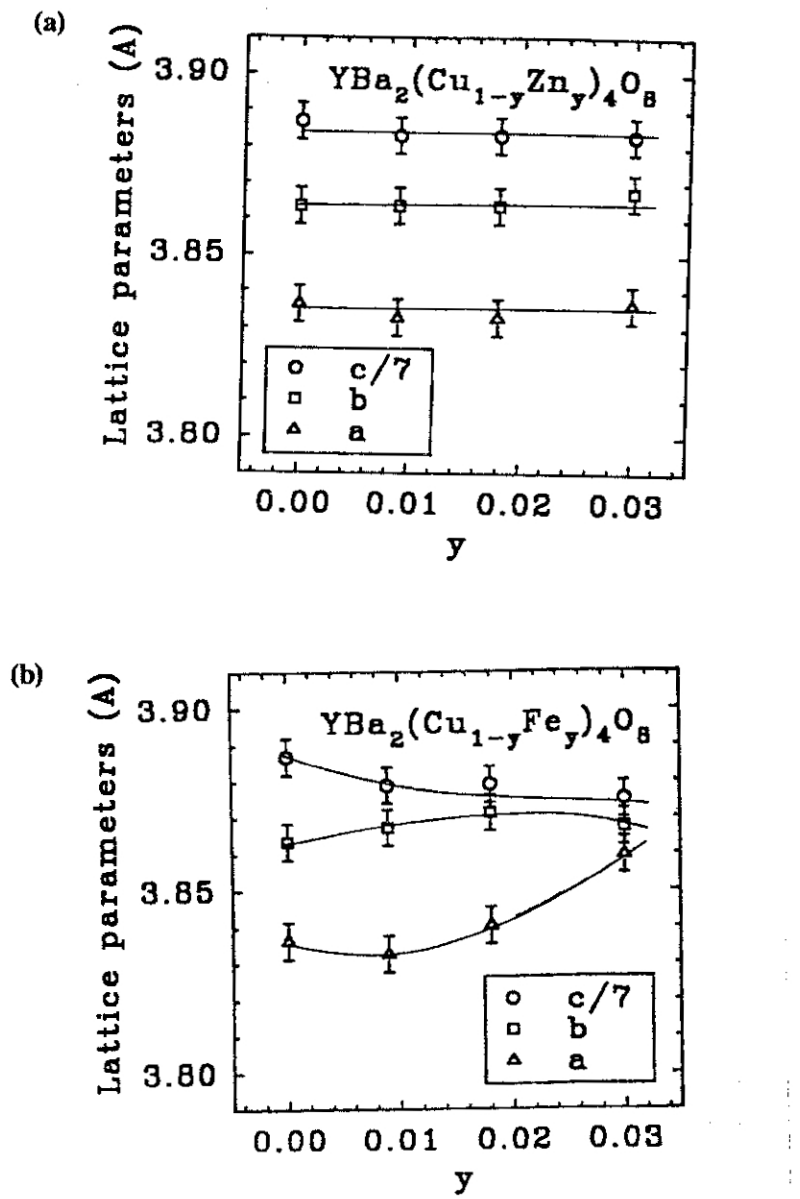


Figure 5. The Lattice Parameters of $YBa_2(Cu_{1-y}M_y)_4O_8$ as a Function of Substitution rate y. (a)M=Zn and (b) M=Fe. The Lines are Drawn to Guide the Eye.

It is now agreed that Co, Al and Ga substitute for the Cu(1) site whereas Ni and Zn go into the Cu(2) site [7,9,13]. In the case of Fe, most substitution occurs onto the Cu(1) site although at higher concentrations Fe substitutes on both Cu(1) and Cu(2) sites [14]. It is noteworthy that the chain site substitutions (Fe, Co, Al and Ga in $YBa_2Cu_3O_{7-d}$ and Fe substitution in $YBa_2Cu_4O_8$) cause a structural change from orthorhombic to tetragonal. This suggests that Fe in $YBa_2Cu_4O_8$ might mostly substitute into Cu(1) site.

A.C. susceptibility measurements of fully oxygenated powder samples of $YBa_2(Cu_{1-x}M_x)_3O_{7-d}$(M=V, Fe, Co, Ni, Zn, Ga and Al) and $YBa_2(Cu_{1-y}M_y)_4O_8$ (M=Fe and Zn) have been performed in order to determine the transition temperatures. The transition temperatures as a function of dopant concentration are plotted in Fig.6(a) for Fe, Co, Ga and Al and in Fig.6(b) for Zn, Ni and V substitution in $YBa_2(Cu_{1-x}M_x)_3O_{7-d}$. All substitutions reduce T_c but with very different rates as given in Table.1. The largest reduction rates are ~7K/% for Zn substitution on the plane site and 5K/% for Co substitution on the chain site. Doping with V slightly reduces the T_c. As seen in Fig.6(a) and 6(b), 3% Ni and Zn substitutions are more effective in reducing the T_c. Transition temperature results presented here are in agreement with literature [12,15,16] to within experimental errors.

Table 1. The Reduction Rates in T_C for a variety of Substitutions in $YBa_2(Cu_{1-x}M_x)_3O_{7-d}$.

Substitution	$DT_c/Dx(K/\%)\pm0.5$
Al	1.5
Ga	2.0
Fe	4.0
Co	5.0
V	0.5
Ni	3.0
Zn	7.0

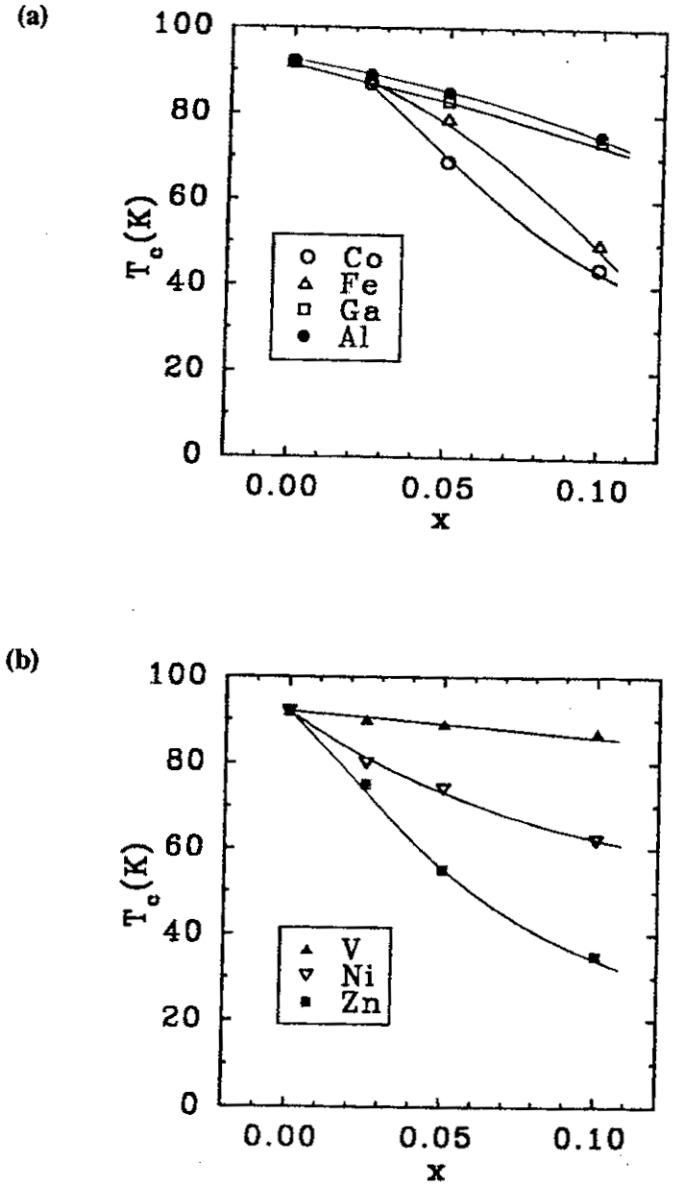


Figure 6. The Transition Temperatures as a Function of Dopant Concentration x for a variety of substitutions in $YBa_2(Cu_{1-x}M_x)_3O_7$. (a) M=Al, Ga, Fe and Co; (b) M=V, Ni and Zn. The lines are drawn to guide the eye

In Fig.7 the transition temperatures determined from A.C. susceptibility measurements are plotted against dopant concentration y in $YBa_2(Cu_{1-y}M_y)_4O_8$ (where M=Zn and Fe and y=0-0.03). Both Fe and Zn substitutions cause a dramatic decrease in T_c with a rate of about 20K/%. The decreases in T_c are much faster than that for Fe and Zn substituted $YBa_2Cu_3O_{7-d}$. These results are in good agreement with those reported elsewhere [12].

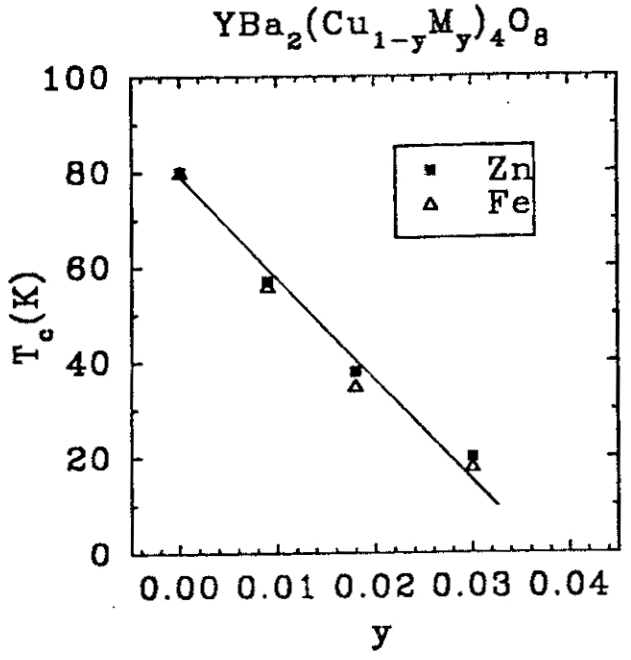


Figure 7. The transition temperatures as a function of dopant concentration y for Zn and Fe substitution in $YBa_2(Cu_{1-y}M_y)_4O_8$. The lines are drawn to guide the eye.

4. CONCLUSION

In summary, Fe, Co, Ga and Al substitutions in $YBa_2Cu_3O_{7-d}$ and Fe substitution in $YBa_2Cu_4O_8$ cause a structural change from orthorhombic to tetragonal. The structure remains orthorhombic for Ni, Zn and V substitution in $YBa_2Cu_3O_{7-d}$ and Zn substitution in $YBa_2Cu_4O_8$. We concluded that all these substitution elements which cause structural change go into chain site. It was found that the decreases in T_c with Fe and Zn substitution for Cu in $YBa_2Cu_4O_8$ are much more rapid than those observed for Fe and Zn substitution for Cu in $YBa_2Cu_3O_{7-d}$.

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