Influence of transition metals substitution on the superconductor $Bi_4Ca_3Sr_3Cu_4O_y$

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Abstract. The results of our investigation on the specimens $Bi_4Ca_3Sr_3Cu_{4-x}T_xO_y$ (T = Fe, Co, Ni, $x \leqslant 0.5$) synthesized in air are presented. Fe and Co substituents result in the formation of $Bi_2Sr_2CuO_y$-type of phase, with considerable depression of T_c of the main phase. However, Ni is completely soluble with Cu in this concentration range without significant depression of superconducting transition temperature (T_c). This difference in the solubility behaviour of Fe and Co on the one hand and Ni on the other is explained taking into account ionic charge and coordination number mismatches.

1. Introduction

The investigation of chemical substitutional effects in high T_c superconductors has contributed to the advancement of knowledge on these oxides. However, the results of such studies on the bismuth-based superconductor, Bi-Ca-Sr-Cu-O are in general quite complicated due to the fact that T_c values differ significantly depending on the value of n in $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ ($n = 1$, $T_c = 10$ K; $n = 2$, $T_c = 80$ K; $n = 3$, $T_c = 110$ K) as well as on the synthetic conditions (Maeda et al 1988; Tarascon et al 1988; Sheng and Herman 1988; Parkin et al 1988; Torardi et al 1988). It is, therefore, absolutely essential to keep the synthetic conditions the same for a meaningful comparison of the characteristics of several chemically-substituted bismuth-based superconductors. The results of such an investigation have been reported by us for some chemical substituents (Sampathkumaran et al 1988; Ikeda et al 1988). Here, we present the results of our investigation to substitute Fe, Co and Ni for Cu in $Bi_4Ca_3Sr_3Cu_4O_y$ (referred hereafter as 4334 phase).

2. Experimental

The samples, $Bi_4Ca_3Sr_3Cu_{4-x}T_xO_y$ (T = Fe, Co, Ni; $x \leqslant 0.5$; y = undetermined) were prepared in air under identical conditions as described earlier (Sampathkumaran et al 1988). X-ray powder diffraction patterns were recorded employing CuK_α radiation. AC susceptibility (χ) and DC resistance (R) were measured in the temperature range 12–300 K in a closed cycle refrigerator (Sumitomo Industries, model SCR 204T). DC χ measurements (4.2–300 K) were performed on selected specimens in a field of about 4 kOe. It may be remarked that some results on nickel specimens have already been published earlier by us (Sampathkumaran et al 1988).

3. Results and discussion

The X-ray diffraction spectra are shown in figure 1 for selected concentrations. The diffraction patterns look similar for $x = 0$ and the nickel specimens, which could be
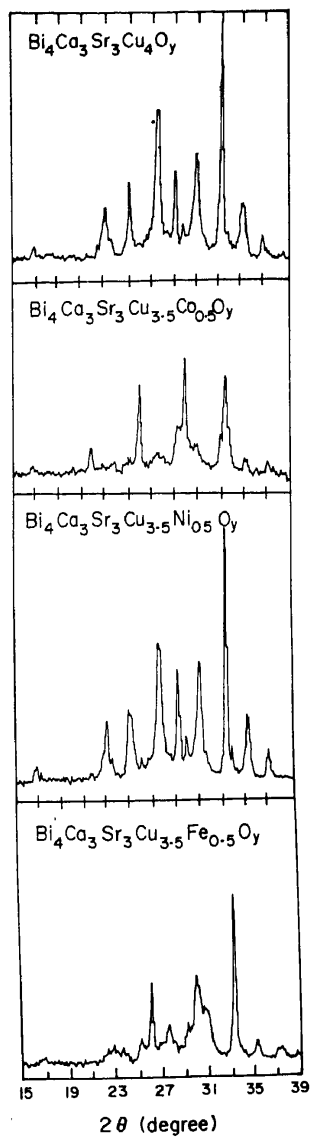
Figure 1. X-ray diffraction pattern (CuK_a) of the specimens, $Bi_4Ca_3Sr_3Cu_{3.5}T_{0.5}O_y$ $(T = Fe, Co, Ni$ and Cu$)$.

indexed on the basis of $n = 2$ phase. However, for Fe and Co specimens, additional lines appear in the X-ray pattern even for small concentrations $(x = 0.1$ and not shown in figure), the intensity of which increases with x. These lines are dominant for $x = 0.5$ (see figure. 1) and could be indexed on the basis of $n = 1$ phase. We have also investigated the diffraction pattern at the low angle region $(2\theta = 3°$ to $8°)$ and the position of (002) line (not shown in figure) is consistent with these conclusions. Thus it appears that nickel could be easily substituted for Cu than Fe and Co. While our work was nearing completion we came to know that Tarascon *et al* (1989a) could not substitute any of
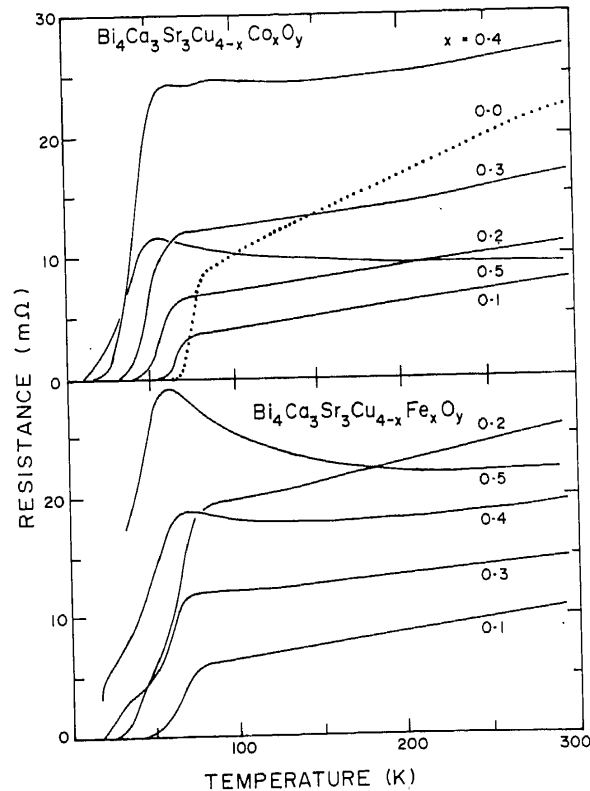
$Bi_4Ca_3Sr_3Cu_{4-x}Co_xO_y$

$x = 0.4$

0.0

0.3

0.2

0.5

0.1

$Bi_4Ca_3Sr_3Cu_{4-x}Fe_xO_y$ 0.2

0.5

0.4

0.3

0.1

RESISTANCE (mΩ)

TEMPERATURE (K)

Figure 2. Resistance as a function of temperature for the specimens, $Bi_4Ca_3Sr_3Cu_{4-x}T_xO_y$ (T = Fe and Co; $x \leqslant 0.5$).

these transition metal ions in $Bi_2Sr_2CaCu_2O_y$ for their synthetic conditions in air, whereas the same group (Tarascon *et al* 1989b, c; Le Page *et al* 1989) reported the formation of $Bi_2Sr_3T_2O_y$ (T = Fe and Co) with more stringent synthetic conditions. These results emphasize the role of heat-treatment conditions, and also possibly Ca/Sr ratios in substitutional effects.

The results of R and a.c. χ measurements on Fe and Co specimens are shown in figures 2 and 3. As remarked earlier (Sampathkumaran *et al* 1988), nickel substitution results in T_c (onset) at about 80 K as in the case of $Bi_4Ca_3Sr_3Cu_4O_y$ for all values of $x \leqslant 0.5$. However, Fe and Co substitution results in the gradual depression of T_c as shown by T_c-onset (defined as the temperature at which R starts decreasing drastically), as well as T_c (the temperature at which $R = 0$ and χ starts becoming negative). For x = 0.5 of Fe and Co series, superconductivity in the temperature range of investigation is not observable as inferred from a.c. χ measurements; the observed drop in R may indicate the existence of small traces of superconducting phase. The systematic decrease of T_c with χ indicates that certain fractions of Fe and Co ions do enter the lattice of (4334) phase, though the X-ray patterns showed the formation of $n = 1$ phase with increasing x. It appears that the effect of Co dopant on T_c is more drastic than that of Fe, possibly due to the higher solubility limit of Co at the Cu site than of Fe under our synthetic conditions.
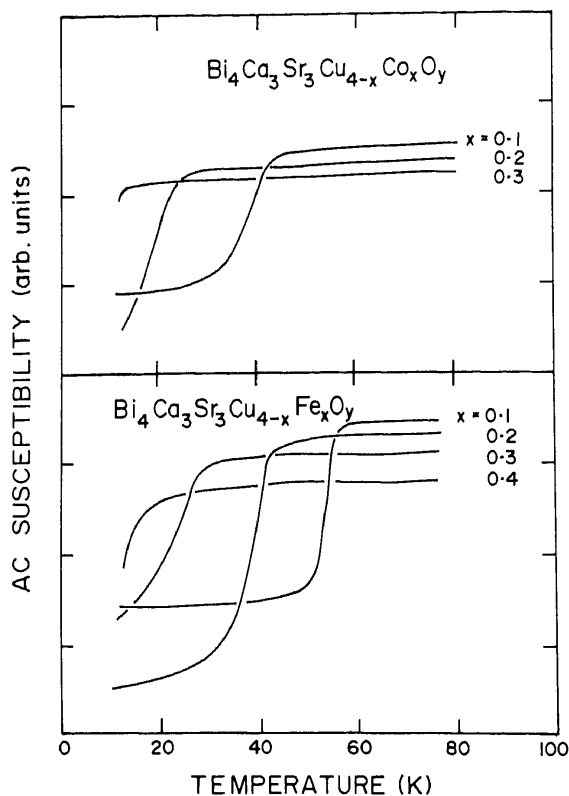
Figure 3. AC susceptibility as a function of temperature for the superconducting specimens, $Bi_4Ca_3Sr_3Cu_{4-x}T_xO_y$ ($T =$ Fe and Co, $x < 0.5$). For clarity, the base line (above 100 K) for all χ is shifted.

We also performed d.c. susceptibility measurements on selected specimens, the results of which are shown in figure 4. We observe a Curie-Weiss behaviour of χ above 100 K for all specimens, with χ increasing as one goes from Ni to Co to Fe. A peak in the χ data around 50 K has been observed for $x = 0.5$. Since Ni specimens are found to be superconducting around this temperature, the drop in χ below 50 K (not shown in the figure) may be due to the dominant diamagnetic contribution $\{(\chi^{-1}$ at 300 K $= 900\,\text{mole/emu}$ and at 100 K $= 525\,\text{mole/emu})\}$. On the other hand, for Fe and Co specimens ($x = 0.5$), this peak may be associated with the antiferromagnetic ordering of transition metal ions in $n = 1$ phase. In support of this, Tarascon *et al* (1989b) have reported antiferromagnetic ordering of $Bi_2Sr_2Cu_{1-x}T_xO_y$ ($T =$ Fe and Co). The results of detailed DC χ studies will be published elsewhere.

4. Conclusion

The results presented in this paper suggest that the attempts to substitute Fe and Co under our preparative conditions in the 4334 phase of the Bi-based superconductor
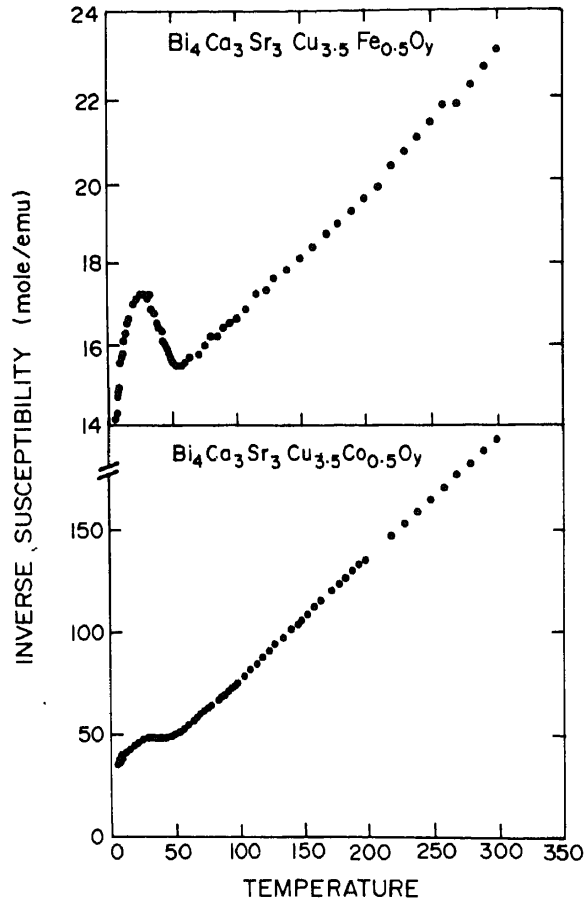
Figure 4. DC inverse susceptibility as a function of temperature (4.2–300 K) for the specimens, $Bi_4Ca_3Sr_3Cu_{4-x}T_xO_y$ (T = Fe and Co).

result in the formation of $n = 1$ phase. However, Ni could be substituted for Cu without this extra phase. The difference in the substitutional behaviour of these T ions may be associated with the valency, size and co-ordination number of mismatches with respect to Cu. Cu is known to be five-fold co-ordinated in the $n = 2$ phase, whereas it is six-fold co-ordinatated in the $n = 1$ phase. It appears that Fe and Co prefer to be trivalent, preferring six-fold co-ordination (Tarascon *et al* 1989a). Therefore, these substituents favour in general $n = 1$ phase under normal heat-treatment conditions. Presumably, Ni and Cu are nearly isovalent, thereby explaining solubility. These views are consistent with the observations noted for the solubility behaviour in $YBa_2Cu_3O_7$ system by several groups. It is generally believed that Co does not occupy Cu in CuO_2 planes (in which Cu is five-fold co-ordinated), but on the chains resulting in the addition of oxygen to make Cu six-fold co-ordinated. However, Ni substitution on the CuO_2 plane in $YBa_2Cu_3O_7$ is possible as noted by us in the bismuth system, due to the fact that Cu in CuO_2 planes is five-fold co-ordinated.

References

Ikeda N, Kohn K, Sampathkumaran E V and Vijayaraghavan R 1988 *Solid State Commun.* **68** 51

Maeda H, Tanaka Y, Fukutumi M and Asano T, 1988 *Jpn J. Appl. Phys.* **27** L209

LePage Y, McKinnon W R, Tarascon J M and Barboux P 1989 (Preprint)

Parkin S S P, Lee V Y, Engler E M, Nazzal A I, Huang T C, Gorman G, Savoy R and Beyers R 1988 *Phys. Rev. Lett.* **60** 2539

Sampathkumaran E V, Vijayaraghavan R, Ikeda N and Kohn K 1988 *J. Phys.* **C18** L163

Sheng Z Z and Herman A 1988 *Nature (London)* **332** 138

Tarascon J M, Le Page Y, Barboux P, Bagley B G, Greene L H, McKinnon W R, Hull G W, Giroud M and Huang D M 1988 *Phys. Rev.* **B37** 9382

Tarascon J M, Barboux P, Hull G W, Ramesh R, Greene L H, Giroud M, Hegde M S and McKinnon W R 1989a *Phys. Rev.* **B39** 4316

Tarascon J M, Miceli P F, Barboux P, Hwang D M, Hull G W, Giroud M, Greene L H, LePage Y, McKinnon W R, Tselepis E, Pleizier G, Eibschutz M, Neumann D A and Rhyne J J 1989b *Phys. Rev.* **B39** 11587

Tarascon J M, Ramesh R, Barboux P, Hegde M S, Hull G W, LePage Y, McKinnon W R, Waszeak J V and Schneemeyer 1989c (Preprint)

Torardi C C, Subramanian M A, Calabrese J C, Gopalakrishnan J, Morissey K J, Askew T R, Flippen R B, Chaudry U and Sleight A W 1988 *Phys. Rev.* **B38** 225