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SUBSTITUTION EFFECTS ON THE T_C OF $RBa_2Cu_3O_z$ (R = Y AND Eu)

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ABSTRACT

We have studied the crystal structure and magnetic susceptibility in single phase samples of high T_c $RBa_2Cu_3O_z$ (where R = Y and Eu) systems in which all the four elements appearing in the formula unit were replaced by different dopants. The T_c for R = Eu is more sensitive to substitutions. When Ba or oxygen are replaced by K^+ or sulfur T_c does not change for R = Y, yet, a progressive decrease in T_c is observed for R = Eu. Partial substitution of Pr for Y or Eu and Fe for Cu leads to the suppression of T_c in both systems, but a sharper decrease of T_c is observed in the case of R= Eu.

INTRODUCTION

The superconducting transition temperature, T_c, of the archetypal, $YBa_2Cu_3O_z$ (T_c – 92K) remains essentially unaltered when Y is replaced by other trivalent magnetic or non-magnetic rare-earth R ions (1) and substitution of K^+ for Ba^{++}, also does not change T_c(2). However, replacing Cu by almost any other element, suppresses T_c. This indicates that the coupling between the magnetic moments of R ions and the superconducting electrons is weak, which, in turn, provides evidence that segregated Cu-O layers and chains are key features of the high T_c in these compounds. Among the rare-earth ions, only the three $RBa_2Cu_3O_2$ compounds with R = Ce, Pr and Tb do not exhibit superconductivitiy, probably because these ions are not trivalent in the $RBa_2Cu_3O_z$ compounds. Partial substitution of Pr for Y leads to the suppression of T_c(4). Eu which belongs to the rare-earth elements like Y which is a 4d transition metal, are both trivalent and nonmagnetic. In order to achieve a better understanding of the role of Y or the rare-earth atoms, and to enlighten their mechanisms, we have prepared several $RBa_2Cu_3O_z$ systems with R = Y and Eu in which all the four elements of the formula were replaced by other dopants, and performed a detailed characterization of T_c as a function of the dopant concentration. Although both pure $YBa_2Cu_3O_z$ and $EuBa_2Cu_3O_z$compounds have the same T_c and crystal structure, the effects of the same dopant on these compounds is quite

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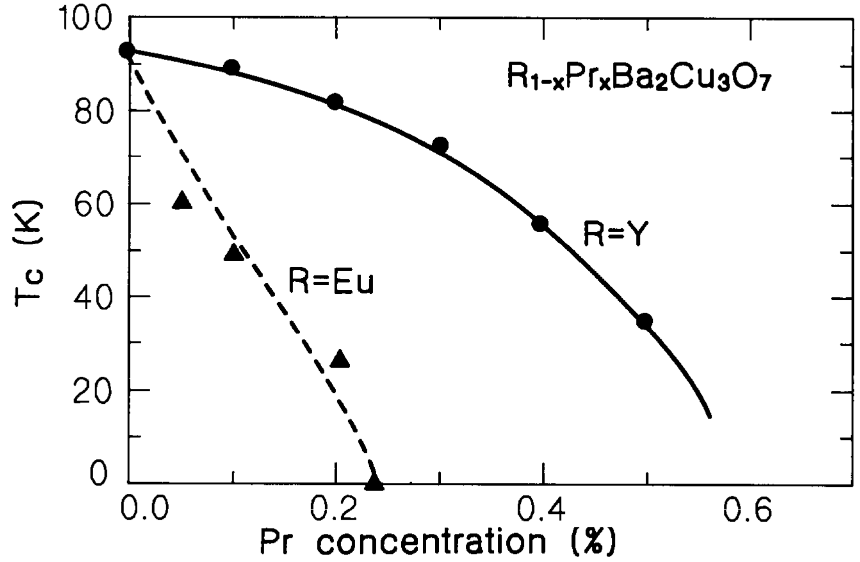

Fig.1. The variation of T_c in $R_{1-x}Pr_xBa_2Cu_3O_z$ with the increasing concentration of Pr.

different. Part of data represented here were published already in our previous papers and the purpose of the present paper is to give a full consistent picture for the dopant effects, and the replacement of all the four elements is discussed. The experimental details on sample preparation and susceptibility measurements which determine T_c, are given in ref. 2 and 3.

RESULTS AND DISCUSSION

1. $R_{1-x}Pr_xBa_2Cu_3O_2$

X-ray diffraction measurements on $Y_{1-x}Pr_xBa_2Cu_3O_Z$ samples revealed that these compounds form the same orthorhombic crystal structure as does $YBaz_2Cu_3O_z$ in which the degree of orthrhombic distortion relative to the corresponding tetragonal structure is diminished upon substitution of Pr for Y(4). The same phenomena occurs in the $Eu_{1-x}Pr_xBa_2Cu_3O_z$ system. When 5% and 10% of Pr is introduced to $EuBa_2Cu_3O_z$ the structure remains orthorhombic with a = 3.860Å, b= 3.5887Å and c = 11.66Å. While increasing Pr to 20% leads to a tetragonal structure with a = 3.889Å and c = 11.69Å;. similar lattice constants are observed for higher Pr concentrations. Fig. 1 exhibits the variation of T_c with increasing Pr concentrations for the $R_{1-x}Pr$ $Ba_2Cu_3O_2$ systems where R = Y and Eu. For R = Y, T_c decreases monotonically with x from 92K at x = 0 to 34K at x = 0.5(4). On the other hand for R = Eu the decrease in T_c is sharper and at x = 0.25 the compound is not superconducting.

2. $RBa_{2-x}K_xCu_3O_2$

Single phase samples with the nominal composition $RBa_{2-x}K_xCu_3O_z$ up to x = 1 have been prepared by introducing monovalent K^+ (K_2CO_3) instead of Ba^{++}. Both ions have similar ionic radii, 1.33 Å and 1.35 Å respectively. For R = Y, a single orthorhombic structure persisted up to x < 1.2. Above this concentration a multi-phase system was observed. Since the ionic radii of Ba^{++} and K^+ are similar, the differences in the lattice parameters are small(2) In the case of R = Eu, a tetragonal structure is induced in K^+ doped samples (even for x = 0.15)(2) and the lattice parameter a, is just the average of the a and b constants of the orthorhombic $EuBa_2Cu_3O_2$ phase. Fig. 2 shows that in $YBa_{2-x}K_xCu_3O_z$, all the samples up to x = 1.0 are superconductors and T_c (= 92-90K) is insensitive to K^+ concentration for x < 0.5 and a small decrease is observed for x = 1, T_c = 89K. On the other hand, a progressive decrease in T_c is observed with increasing x in $EuBa_{2-x}K_xCu_3O_z$, leading ultimately to a non-superconducting compound $EuBaKCu_3O_z$. The Eu is in a pure trivalent state for all these compounds. It is usually assumed that the average valence of Cu in all the $RBu_2Cu_3O_z$ exceeds 2. We have shown (2) that the decrease in the cation charge when Ba^{++} is replaced by K^+, reduces the oxygen concentration in both $RBa_{2-x}K_xCu_3O_z$ systems in the same manner. The reason for the difference of the curves in Fig. 2 is not yet clear

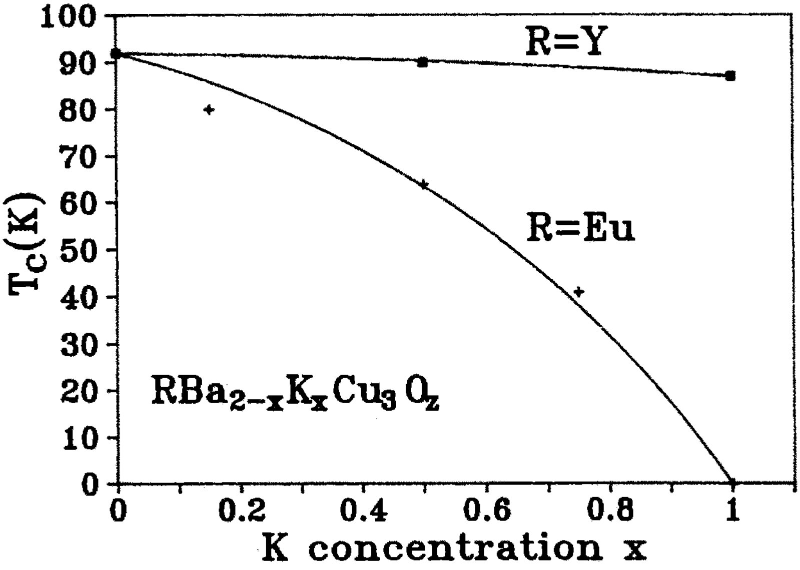

Fig 2. The dependence of T_c with K^+ concentration in the $RBa_{2-x}K_xCu_3O_z$ systems.

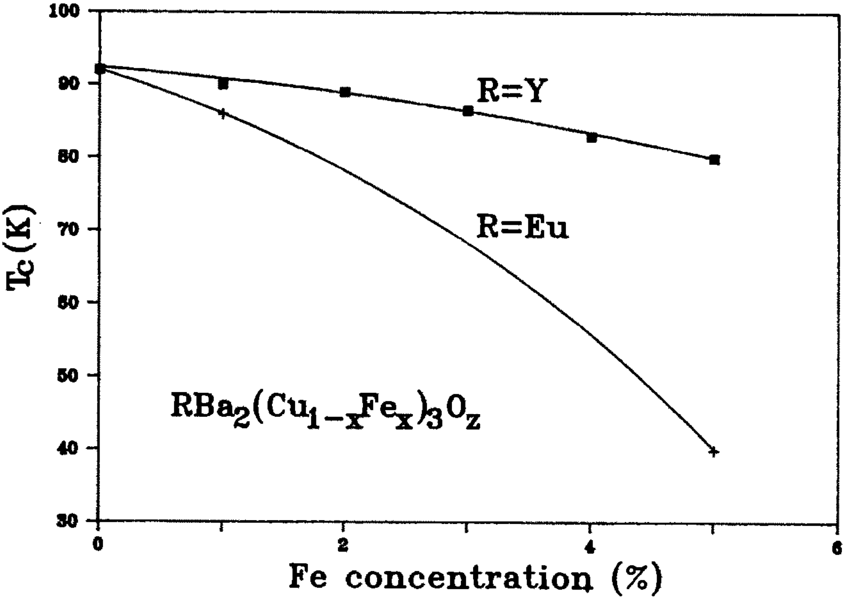

Fig. 3. The decrease of T_c with Fe concentration in $RBa_2(Cu_{3-x}Fe_x)_3O_z$.

3. $RBa_2(Cu_{1-x}Fe_x)_3O_z$ and $RBa_2Cu_3O_6S$

The effect on T_c of Fe substitution for Cu in $YBa_2Cu_3O_z$ was discussed by several authors(3,5-6). It is well accepted that replacing Cu for Fe suppresses T_c, and for x >0.03 the crystal structure changes from orthorhombic to tetragonal. But, there is disagreement among the authors on the exact suppression of T_c with x. The effect of Fe on the T_c of $EuBa_2Cu_3O_z$ is given here for the first time. In this system 1% of Fe is sufficient to change the orthorhombic structure to a tetragonal, and the lattice parameters obtained for 1% and 5% Fe doped in $EuBa_2Cu_3O_z$ are: a = 3.901Å and 3.892Å and c = 16.76Å and 16.67Å respectively. Fig. 3 shows the concentration dependence of T_c for both systems, where the values for R = Y are the average T_c values taken from ref. 3, 5-6. Here again, one definitely sees the difference between the two systems where T_c drops rapidly in the case of R = Eu.

As a final point of interest we may add, that substitution of oxygen by sulfur in $YBa_2Cu_3O_2$does not change T_c and the crystal structure for $YBa_2Cu_3O_6S$ remains orthorhombic with some expansion in the lattice parameters, which indicate that the bigger sulfur atoms really replaced oxygen(2). In the case of $EuBa_2Cu_3O_z$, substitution of oxygen by sulfur decreases T_c (= 85K) and the crystal structure for $EuBa_2Cu_3O_6S$ is tetragonal(7).

CONCLUSIONS

The observations reported in the present paper lead to the following conclusions. 1. Although both pure $RBa_2Cu_3O_z$ compounds, R = Y and Eu have the same T_c, the same dopant has different effects on these compounds. 2. It is possible to replace all the four elements in both systems by other elements. 3. No significant effect on T_c occurs in $YBa_2Cu_3O_z$ when Ba^{++} and oxygen are substituted for K^+ or sulfur, whereas in $EuBa_2Cu_3O_z$ T_c is decreased by such substitution. 4. Partial substitution of nontrivalent Pr for R or Fe for Cu leads T_c to decrease monotonically in both systems, and for R = Eu the depression of T_c as a function of the dopant concentrations appears to be faster. The reason for the difference between the two systems is still unclear, but it is assumed that the difference in the electronic structure of Y (3d element) and Eu (4f element) plays an important role on the superconducting properties of the systems.

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