

DOPING EFFECT ON THE D.C. ELECTRICAL RESISTANCE OF
THE HIGH TEMPERATURE SUPERCONDUCTING
Y - Ba - Cu - O SYSTEM

BY

M. EL-ZAIDIA

Physics department, Faculty of science,
Menofia university, Shebin El-Kome, Egypt.

AND

A.A. EL-HAMALAWAY AND M.A.T. DAWOUD

Physics and mathematics department,
Faculty of electronic engineering
Menofia University, Menof, Egypt.

ABSTRACT

The effect of doping the high temperature superconducting system Y-Ba-Cu-O with metals (Ag) is analysed. A series of alloyed specimens of the system $(Y_{1-x}Ag_x)Ba_2Cu_3O_{7-s}$ with $x=0.0, 0.02, 0.04, 0.06, 0.08$ and 0.1 were prepared. The D.C. Electrical resistance has been measured against temperature in the range from 77°K to 300°K.

The doping, generally, increases the critical temperature T_c at which the D.C. electrical resistance falls to zero, but this increase is not monotonous. The doping also decreases the normal state resistance monotonously. In order to throw some light on this behaviour X-ray diffraction patterns for the samples were obtained.

INTRODUCTION:

The number of publications in the last three years in the field of superconductivity is more than hundred times that in the previous 75 years since the discovery of superconductivity in Hg at $T_c = 4.15^\circ K$ by Onnes in 1911.

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The discovery of superconductivity with $T_c = 30^\circ\text{K}$ in the oxide La - Ba - Cu - O by Bednorz and Muller [1] in 1986 has attracted the attention of all the scientists interested in the field of superconductivity. This has been followed by a flood of intensive research to understand the phenomenon and characterize the materials or to look for new materials. Then Zhao et al [2] and Chu et al [3] have started a new Era by the discovery of the first high temperature superconducting system Y-Ba-Cu-O with $T_c = 92^\circ\text{K}$, which can be used at liquid nitrogen temperature for the first time.

Then the research for increasing the T_c for the systems La-Ba-Cu-O [4] and Y-Ba-Cu-O [5] has soon followed, and we have participated in this race [6 - 12]. One of the techniques used to increase the T_c in those known compounds is doping with different elements.

Y. Saito et al [13] has studied the system $(\text{Ba}_{0.1}\text{La}_{1.9})\text{Ag}_x\text{Cu}_{3-x}\text{O}_{7.5}$ and reported that a small Ag amount with $x < 0.1$ increases the T_c with respect to pure parent system (see fig. (1)). Another results obtained by the same author [14] show that T_c decreases for $x > 0.1$ in the system $\text{Y}_1\text{Ba}_2\text{Cu}_{3-x}\text{Ag}_x\text{O}_{7.5}$ system.

This had led us to investigate a series of alloyed compound $(\text{Y}_1\text{Ba}_2\text{Cu}_{3-x}\text{Ag}_x\text{O}_{7.5})$ with different values x from 0.0 to 0.1 in which copper sites in the compound are partially occupied by Ag atoms. We report here the results of the D.C. electrical resistance measurements which allows a direct

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into pellets for the final sintering at 940 °C in a flow of air for 12 hours. The pellets were cooled down to room temperature with a cooling rate of 150 °C/h.

Part of each sample was successfully checked for superconductivity using magnet levitation at liquid nitrogen temperature. And orthorhombic phase was confirmed by X-ray diffraction patterns using Cu K α - radiation as shown in figures (2,3 and 4) for all the samples.

D.C. Electrical Resistance results, figure (5), were obtained using the four-probe technique with light pressure contact electrodes at 5 mA using Keithly constant current source. The voltage drop was measured using Keithly nanovoltmeter. The sample was inserted in a liquid nitrogen cryostat under vacuum. The temperature was detected simultaneously by platinum resistance thermometer PT-100 with an accuracy +/- 0.1 °K. All the measurements were controlled by using PC computer.

RESULTS AND DISCUSSION:

X-ray diffraction patterns were obtained for the six samples. The diffraction patterns do not show extra phases other than the dominant phase Y₂ Ba₂ Cu₃ O_x [15&16] at the lower percentages of Ag, but on increasing Ag content an extra peak around 2 θ = 39° starts to develop and it belongs to the pure Ag phase [13 & 14]. Comparing the X-ray patterns with other patterns representing the phase 123 YBCO [15 & 16], shows that for small values of x some

copper sites are actually substituted by Ag ions to form new alloyed compound system $(Y_1 Ba_2 Cu_3)_{1-x} Ag_x O_{7.5}$. This has been confirmed since there was no change in the detected ideal phases (13 & 14).

Temperature dependence of the reduced resistance for the samples with x equals 0.0, 0.02, 0.04, and 0.08 are shown in figure (5). The data show that the resistance linearly decreases with the decrease in temperature from 300°K to 100°K for all samples under investigation, which means that they show metallic behaviour. In general doping increases the critical temperature " Tc " and the positive temperature coefficient, but it should be pointed out that the increase of Tc was not monotonous. The sample with x = 0.02 shows a higher Tc than the other compositions. This composition also shows a sharp superconducting transition region which is as narrow as 3°k compared with other compositions, figure (6). This indicates that the orthorhombic phase occupies the most of sample matrix volume.

Although in other work [10] for similar compounds prepared with different technique and measured under 100 mA A.C. current, the highest Tc was reported at 4% Ag concentration, which reflects the fact that this class of materials is very sensitive to the method of preparation.

In figure (6) the Tc superconducting transition temperatures are plotted versus Ag concentrations (x). It is

interesting to notice that T_c values increase with small concentrations of Ag. This figure also shows that the samples with $x = 0.04$ and 0.08 are found to be superconducting and that T_c 's are very close to each other.

We may say that doping the high temperature superconducting system YBCO with a small percentage of silver increases the T_c and leads to a better superconductor and the best detected superconductivity is obtained at $x = 0.02$. Increasing the percentage of silver above 10% will lead to a decrease in the T_c value [14]. Introduction of monovalent silver in place of mixed valent Cu is expected to cause large charge imbalance which may modify the Cu^{3+}/Cu^{2+} ratio, because the T_c is very sensitive to this ratio and increases with it [17 and 18].

In the oxide superconducting system Y-Ba-Cu-O the Cu appears in two sites, the first site is trivalent Cu^{3+} and is directly responsible for the superconductivity and the other site is divalent Cu^{2+} and is indirectly related to the superconductivity [19]. That is why it is expected that when a small fraction of foreign metal, like Ag, substitutes the Cu^{2+} , T_c increases slightly, but on increasing the Ag higher than 10% it may occupy the Cu^{3+} site which consequently decreases the T_c . Moreover according to the many body theories of the cuprate superconductors [18] when a small fraction of divalent Cu^{2+} in the parent compound is replaced by a monovalent silver, charge balance requires that electrons be taken away (or holes added to) Cu-O planes. The added holes are mobile and they are responsible

for the superconductivity.

This can be interpreted in terms of the superconducting electrons which may be formed by the created holes with the excess electrons of monovalent silver to create electron - hole symmetry. This condition operates well till the monovalent Ag electrons attack the Cu^{2+} site to reduce the probability of forming superconducting electrons, this in turn reduces the T_c above 10% Ag concentration.

CONCLUSION:

We may conclude that doping the high temperature superconducting system Y - Ba - Cu - O with small percentages of silver up to 2% will increase the T_c but heavily doping with higher percentages will lead to a decrease in the T_c .

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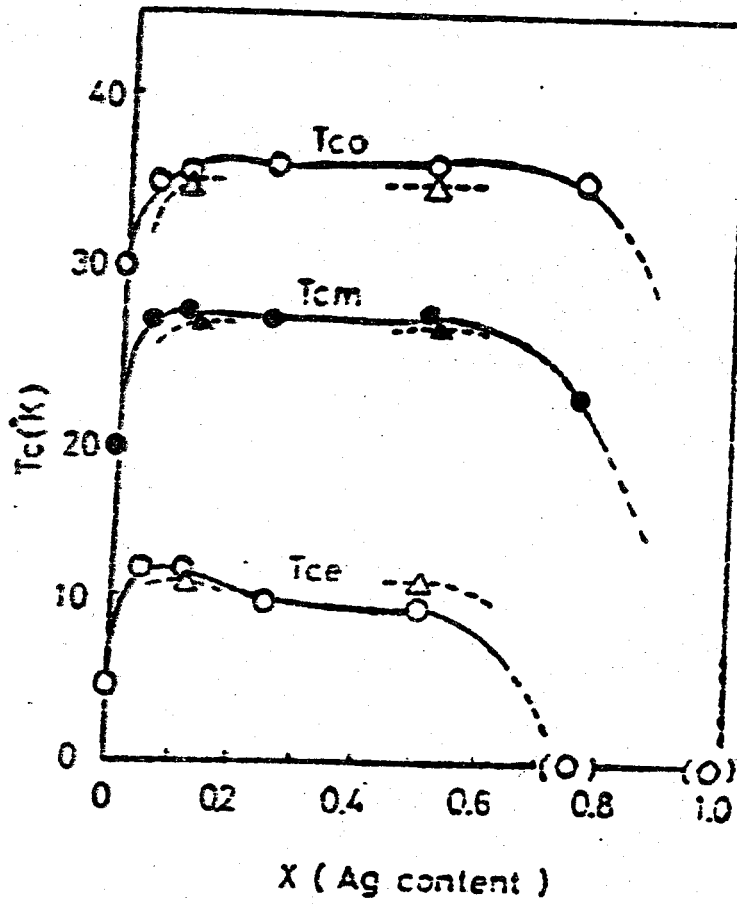


FIGURE (1)

Superconducting transition temperature as a function of Ag content, when sintered at 1050 °C (circle) and at 1000 °C (triangles). The measured points parenthesized on the abscissa mean non-superconductivity above 1.5 °K.

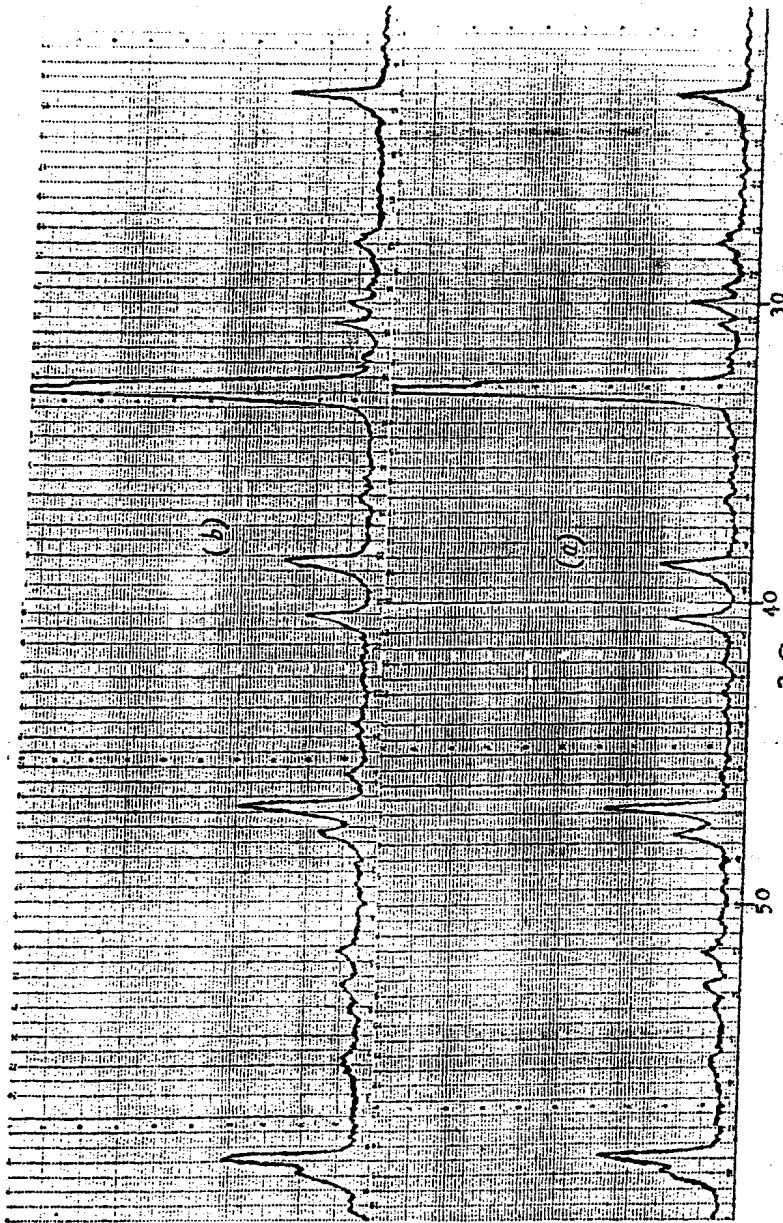


FIGURE (2)
X-ray diffraction patterns for the system under investigation;
a) $x = 0.00$ b) $x = 0.02$

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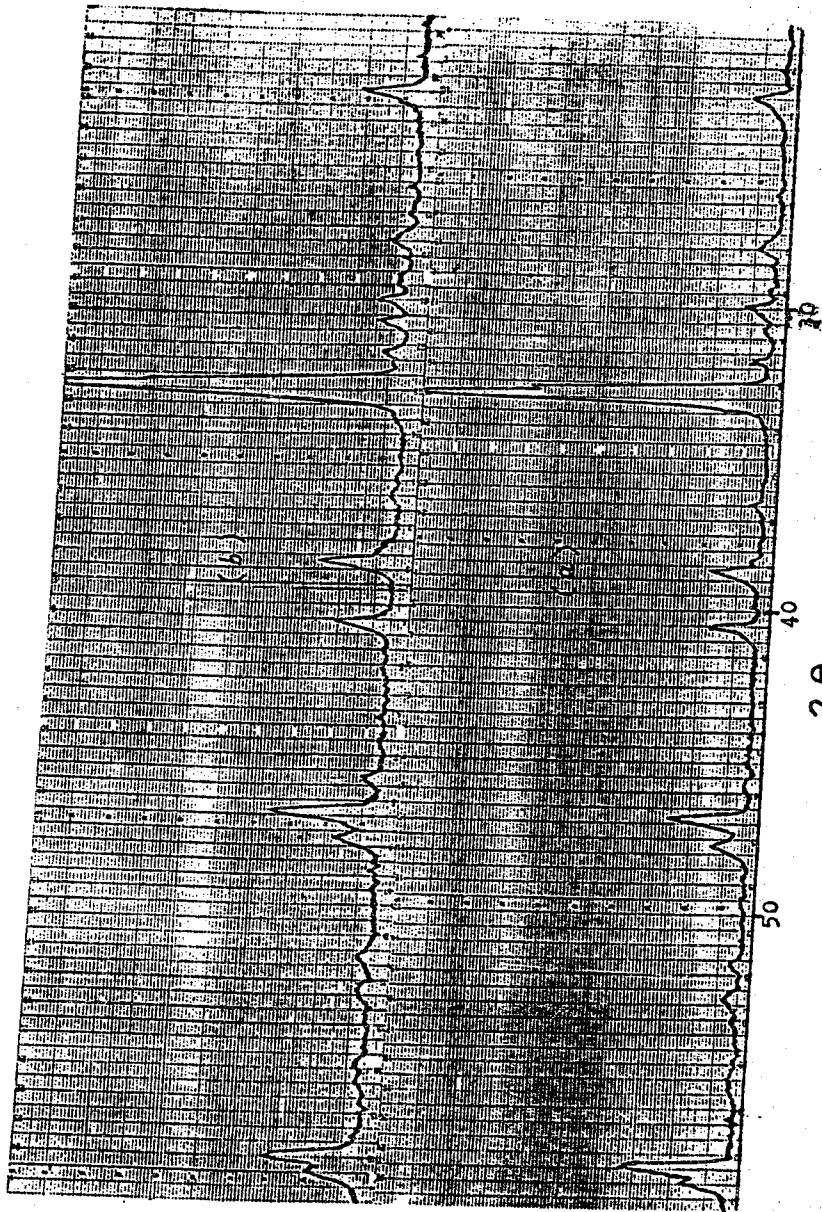


FIGURE (3)

X-ray diffraction patterns for the system under investigation;
a) $x = 0.04$ b) $x = 0.06$

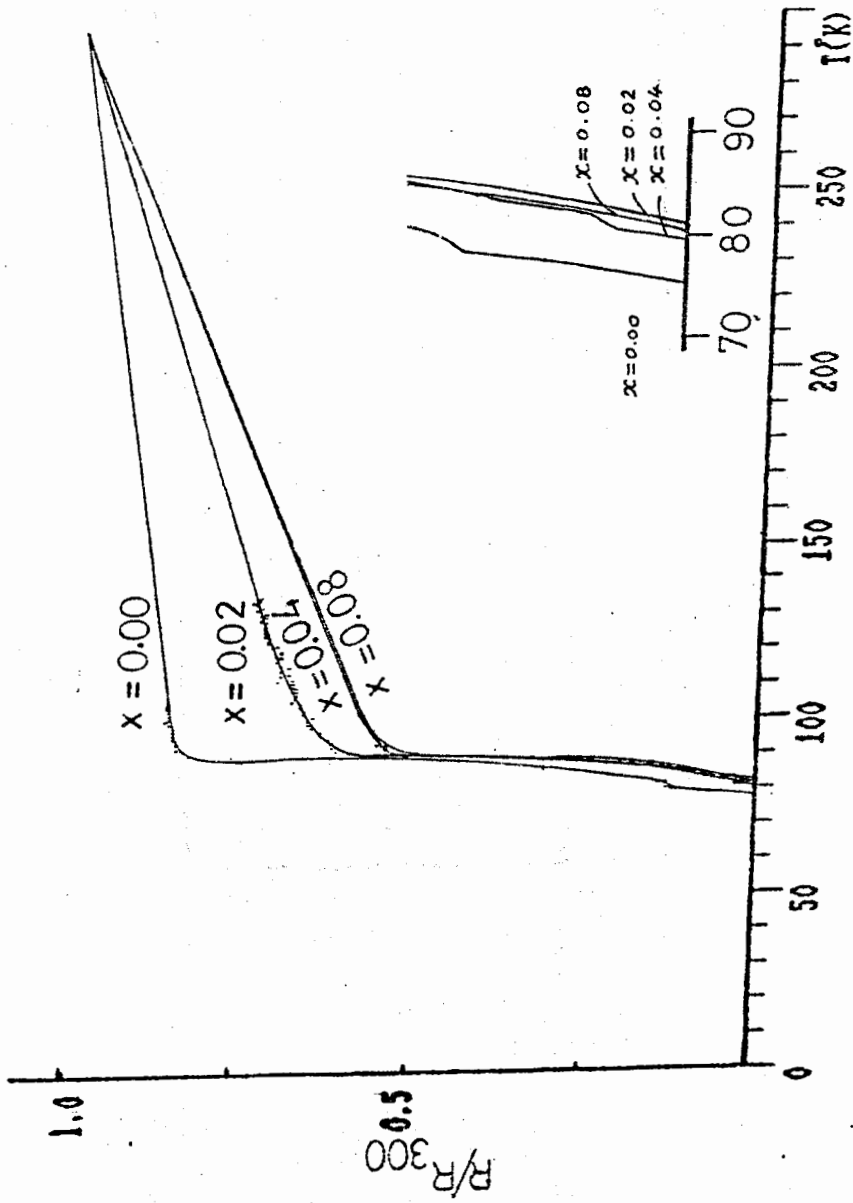


FIGURE (5)
Reduced D.C. electrical resistance for the system under
investigation;

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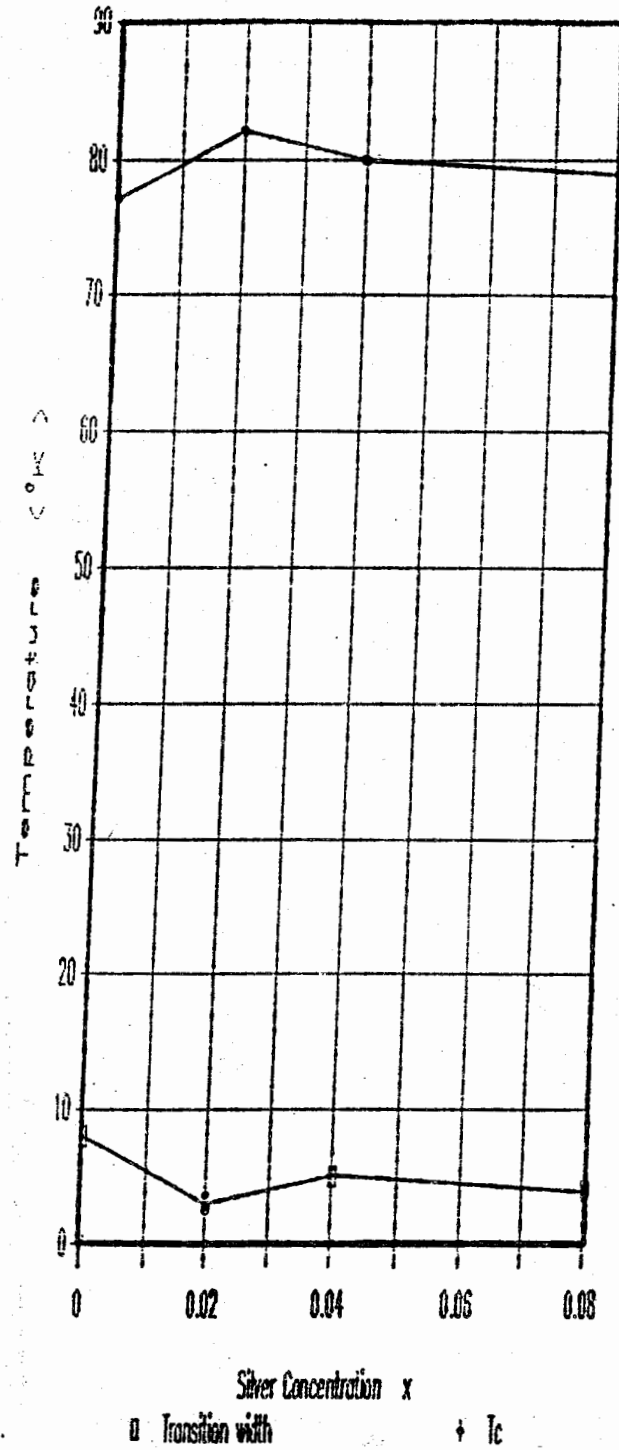


FIGURE (6)

The parameters of the superconducting transition temperature T_c as a function of the silver content in the system under investigation.