

STRUCTURE, SUPERCONDUCTIVITY CHARACTERIZATION  
AND Fe MOSSBAUER STUDIES ON HIGH TEMPERATURE SUPERCONDUCTOR  
 $Y_1 Ba_2 (Cu_{3-x} Fe_x) O_{7-6}$

BY

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ABSTRACT

Different samples of  $Y_1 Ba_2 (Cu_{3-x} Fe_x) O_{7-6}$  compounds have been synthesized, the resultant bulk superconductors were found to show diamagnetic behaviour and they have been investigated from the point of view of superconductivity through the study of X-ray diffraction, A.C. magnetic susceptibility, electrical conductivity and Mossbauer effect.

INTRODUCTION

Investigations by Bednorz and Muller [1,2] opened a new direction in the field of high temperature superconductivity " $T_c$ ". A great advances have been made in achieving superconductivity at higher temperatures [3,4] in materials with and without rare-earth elements such as  $Y_1 Ba_2 Cu_3 O_{7-6}$  with  $T_c$  about 92°K [5], which became a standard superconducting materials.

Superconductivity has already been found in cases of several metallic oxide materials [6,7], and a great efforts have been made to study the relationship between their structure and superconductivity. Structure and structural changes in high  $T_c$  superconducting materials can not be detected by diffraction

methods easily at the superconducting transition temperature. On the other hand the A.C. magnetic susceptibility and the electrical resistivity changes dramatically, and also a study using the Mossbauer effect (M.E.) spectra may give informations about the microscopic behavior of probe atoms at the superconducting transition temperature.

In order to shed more light on that sense, the M.E. spectra were collected for different Fe concentrations doped in  $Y_1Ba_2Cu_3O_{7-\delta}$  system, at different temperatures. Iron ( $^{57}Fe$ ) was chosen as substitutes of copper.

#### EXPERIMENTAL WORK

The starting materials were  $Ba(NO_3)_2$ ,  $CuO$  and  $Y_2O_3$  powder with a purity over 99.9%. The samples under investigation have the nominal composition  $Y_1Ba_2Cu_{3-x}Fe_xO_{7-\delta}$  and were prepared by the conventional solid state reaction method [8] as in the following steps:

##### 1-Preparing the barium cuprates:-

$Ba(NO_3)_2$  and  $CuO$  powder were mixed together, pressed at 600  $Kg/cm^2$ , heated at 950° C for 1 hour, cooled with a rate of 150° C/h, and finally the resultant material was grained.

##### 2-Preparing the $Y_1Ba_2Cu_3O_{7-\delta}$ :-

$Ba_2Cu_3O_9$  and  $Y_2O_3$  powder were mixed, pressed to 600  $Kg/cm^2$ , heated at 950° C with a slow flow of air for 5 hours, cooled to 200° C with cooling rate 150° C/h, the sample is then

cooled to room temperature in air, grounded and pressed to 600 Kg /cm<sup>2</sup> and heated at 950° C in a flow of air for 1 hour and left to cool with a rate of 100° C/h.

### 3-Preparing the suggested compositions:-

The iron ( <sup>57</sup>Fe ) enriched up 80% was introduced in the form of Fe<sub>2</sub> O<sub>3</sub> powder. Y<sub>1</sub> Ba<sub>2</sub> Cu<sub>3</sub> O<sub>7-δ</sub> and Fe<sub>2</sub> O<sub>3</sub> were mixed together with different ratios to verify the Y<sub>1</sub> Ba<sub>2</sub> Cu<sub>3-x</sub> Fe<sub>x</sub> O<sub>7-δ</sub> system where x ranges from 0 to 0.08. The powders were heated into pellets for the final sintering at 900° C in a flow of air for 12 hours. The pellets were cooled down to room temperature with cooling rate of 150° C/h.

The diamagnetic properties of the samples have been checked by observing Meissner effect, using the elevating magnet technique, this has been done using a part of the pellets. Indications showed that the composition with x=0.08 does not show appreciable diamagnetic effects.

The crystal structure of the high T<sub>c</sub> compounds with different iron concentration have been analyzed by using x-ray diffractometer (Cu Kα). Fig (1) shows the x-ray patterns for the most characteristic peak around 2θ = 33° . The figure shows the orthorombic-tetragonal transition as a function of the amount of iron-dopping.

D.C. electrical conductivity data; Fig(2); were obtained by the four-probe technique using silver paste electrodes and a constant current 10 mA source. The voltage drop was detected

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using an accurate voltage amplifier followed by a digital millivoltmeter. The temperature was measured simultaneously by a copper-constantan thermocouple.

The A.C. magnetic susceptibility was measured by the double-coil method. The A.C. magnetic susceptibility in terms of  $\chi'$  (real part) was measured as a function of temperature for different Fe-ionic concentration as shown in figure (3).

The M.E. spectra for both different temperatures and different iron-atomic concentration were collected in figs. (4 & 5) using a constant acceleration driving system, transmission geometry M.E. spectrometer and the absorber which was situated in a L.N. cryostat. The temperature being controlled with an accuracy of  $\pm 1^\circ\text{K}$ , and the source used was  $^{57}\text{Co}/\text{Pd}$  with intensity of 50 mCi.

#### RESULTS AND DISCUSSION

The most characteristic peak of the x-ray pattern for  $\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{Fe}_x\text{O}_{7-s}$  with  $x=0.08$  shows that it is very difficult to find the orthorhombic phase [9,10,11]. This sample does not show any superconducting transition through A.C. magnetic susceptibility or D.C. conductivity measurements, which suggest that the orthorhombic-perovskite related structure is responsible for elevating the superconducting transition temperature  $T_c$ .

Powder X-ray diffraction showed that for higher Fe-doping more tetragonal-orthorhombic transition is detected. To check the

order-disorder transition in detail the most characteristic peak which differentiate these two structures have been analyzed for different Fe-doping. At  $x=0.06$  there is a mixture of the two phases but the tetragonal phase is dominating, as observed from the study of the overlapped peaks with indices (110,103) and (013) with diffraction angles  $2\theta = 33.1^\circ, 32.7^\circ, 32.9^\circ$  and  $33.6^\circ$  [10,11].

Figure (2) shows the temperature dependence of the normalized resistance to the value at  $300^\circ\text{K}$ , in the temperature range from  $80^\circ\text{K}$  to  $200^\circ\text{K}$ . From the D.C. conductivity results, it can be seen that the most interesting behaviour of the sample with  $x=0.06$ , doesn't exhibit zero resistance in the whole temperature range, but there is a sharp drop at a temperature of  $100^\circ\text{K}$  which corresponds to  $T_c$  for the pure sample ( $\text{Y}_1\text{Ba}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7-5}$  with  $x = 0.00$ ). Thus we can conclude that the sample with  $x=0.06$  contains a semimetallic phase besides the superconducting one. But according to the percolation theory of conductivity, the sample does not show zero resistance as an superconducting behaviour. On the other hand, checking the diamagnetism at  $77^\circ\text{K}$  proves the existence of the superconducting phase with volume fraction, estimated to be as the pure sample with  $x = 0.00$ .

From the structure and electrical behaviour of all samples with  $x = 0.00$  to  $x=0.06$ , it was found that by increasing the Fe-concentration, the structure was changed from orthorombic to tetragonal structure. Also the superconducting transition

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temperature  $T_c$  decreases by increasing Fe-atomic concentration.

Fig(3) confirms the existence of a superconducting phase in the present samples. The superconducting transition temperature measured from this figure agrees with  $\pm 2^\circ\text{K}$  of the  $T_c$  value obtained from Y - Ba - Cu - O sample with  $x=0.00$ . Also Fig(3) represents some superconducting materials having different  $T_c$  for samples with  $x=0.06$  which may be distributed in the form of discrete fine grains.

All the spectra of M.E. show a lack of magnetic splitting of the Fe-doped  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  samples which might demonstrate that the iron atoms are built into the structure of perovskite. One can distinguish the spectra as two quadrupole doublets, that were associated with the two distinct environments of the Fe atoms in the Cu planes. The isomer shift calculated from the M.E. spectra (about  $+0.05$  mm/s) might be interpreted as a low spin Fe II or Fe III state [12]. Fig(4) shows the M.E. spectra at different Fe-ionic concentrations. It will be seen that iron enters two planes (the outer peaks are related to the  $\text{Cu}_2$  plane; which suffers more deformation i.e. more quadrupole splitting; and the inner doublet is related to the  $\text{Cu}_1$  plane). Thus in the orthorhombic structure; where excess oxygen atoms make asymmetrical distortion in  $\text{Cu}_1$  plane; we can conclude that the Fe ion suffers anisotropy in its vibration which is responsible for the superconductivity phenomena.

The dependence of the shape on the temperature for the

composition with  $x=0.04$  is clear from fig.(5). The behavior of the inner doublet; which is responsible for the superconductivity phenomena; demands that its behaviour is temperature dependant. The anisotropy of the M.E. spectra confirms this suggestion and lead us to coclude that the superconducting phase suffers from Goldanskii-Karyagin effect [13], where such strong anharmonic vibration are specific features of the perovskite stucture [14]. Where the instability of the central location of the anion at a face of the stucture determines a local double potential, each of these two components are affected with different values by varying the temperature.

Below the  $T_c$  an interisting change in the spectra could be observed, and may be explained as due to the softening of the structure by some mechanisms [15]. At lower temperatures a further and extended study of this phenomenon is under progress.

We can conclude that by increasing Fe-atomic concentration, more orthorombic-tetragonal transition and more reduction in the superconductivity transition temperature, are observed. Mossbauer spectra depend on the Fe concentration and temperature.

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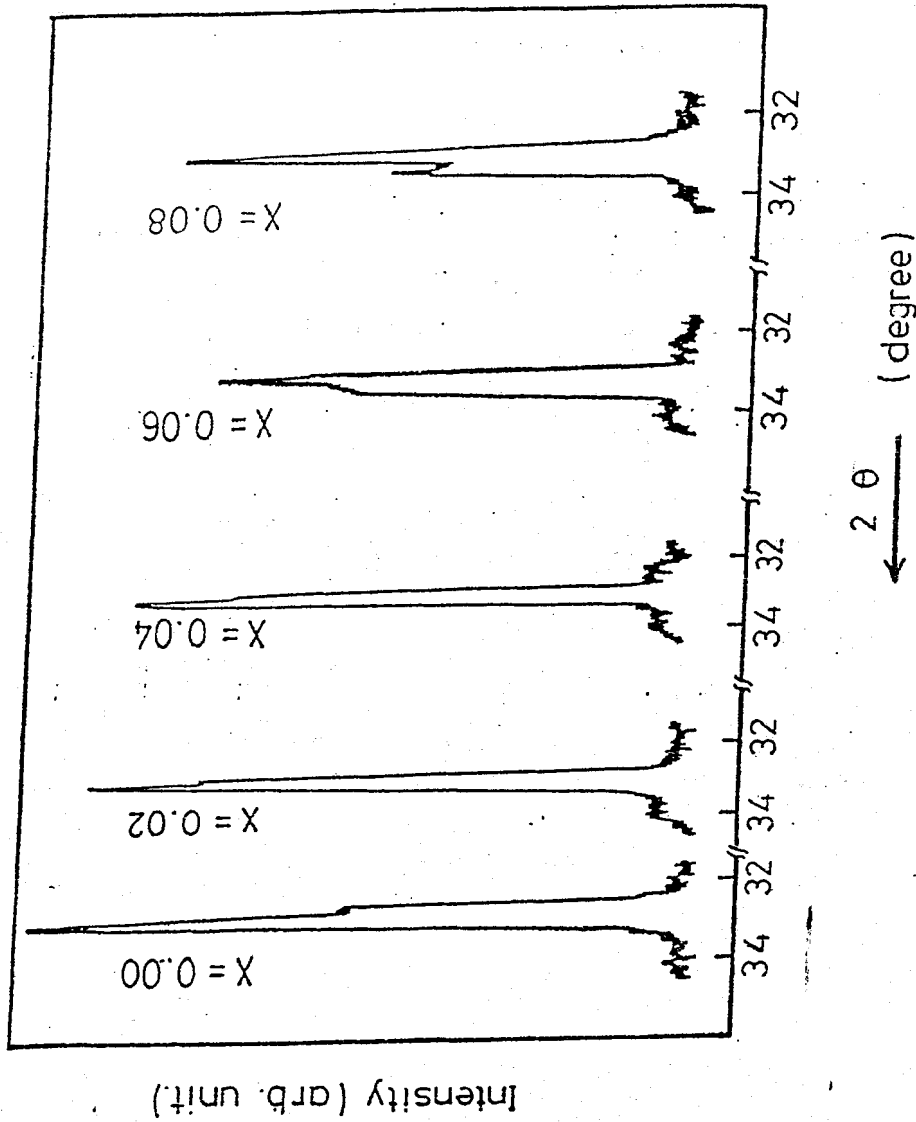


Fig. (1) X-Ray diffractogram of the most characteristic peak around  $2\theta = 33^\circ$  for  $Y_{1-x}Ba_2Cu_{3-x}Fe_{2-x}S$  system at different values of  $x$ .

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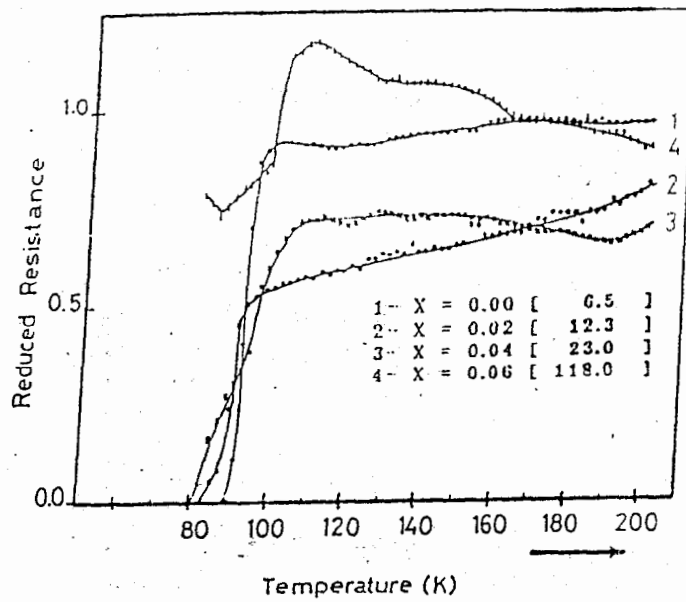


Fig. (2) Resistance; normalized by its value at 300oK; as a function of. temperature for  $Y_1 Ba_2 Cu_{3-x} Fe_x O_{7-\delta}$  at different values of x. Typical values for the resistivity of the samples at room temperature in  $m\Omega \cdot cm$  are shown between brackets.

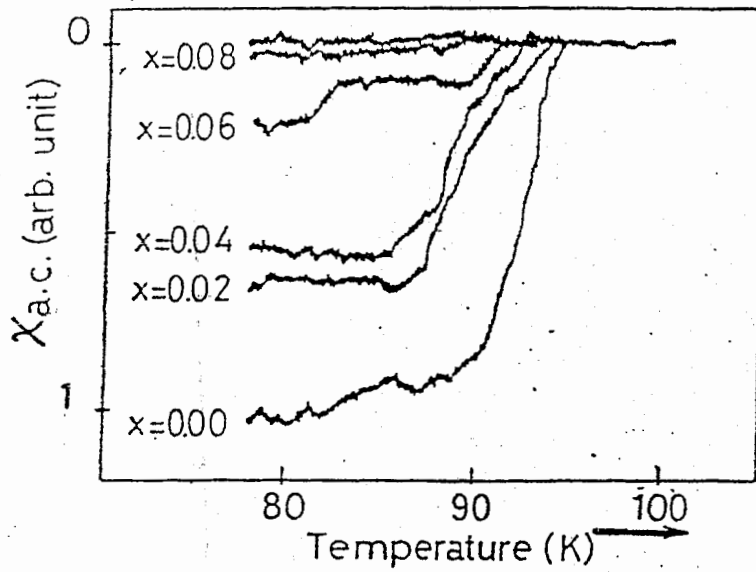


Fig. (3) Typical behaviour of the a.c. magnetic susceptibility ( $\chi$ ) as a function of temperature in  $Y_{1-x}Ba_2Cu_3F_xO_{7-\delta}$  superconductor system at different values of  $x$ .

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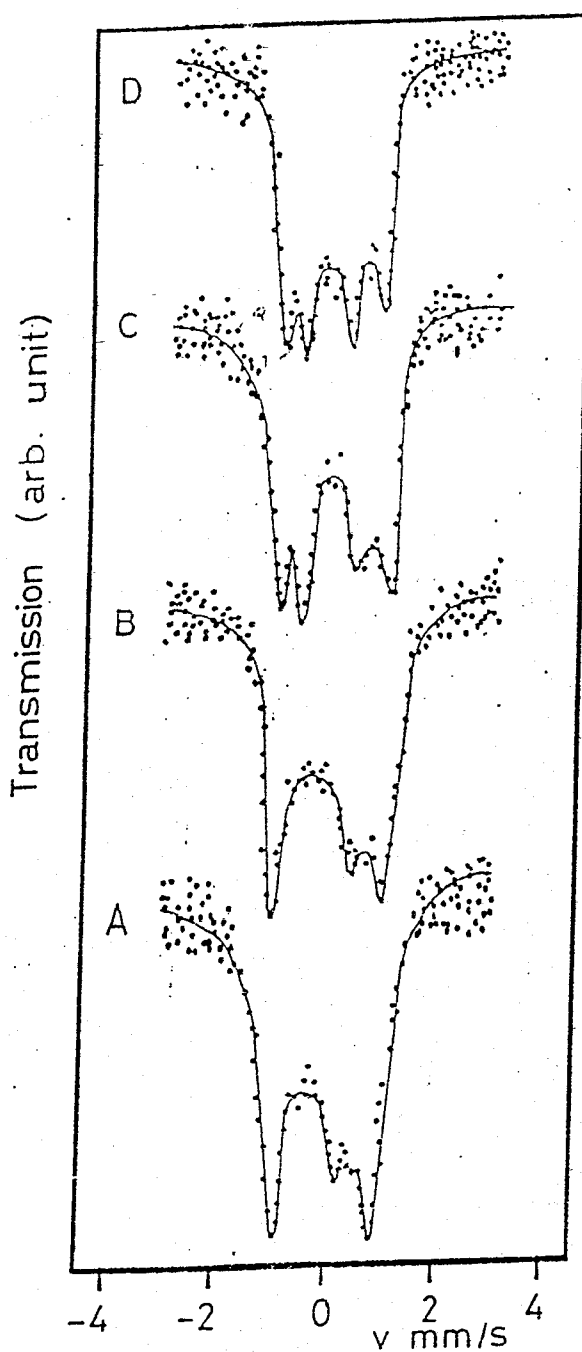


Fig. (4)  $^{57}\text{Fe}$  Mossbauer spectra for the  $\text{Y}_1\text{Ba}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_7\text{-S}$  system with  $x = 0.02$ (A),  $0.04$ (B),  $0.06$ (C) and  $0.08$ (D) measured at room temperature.

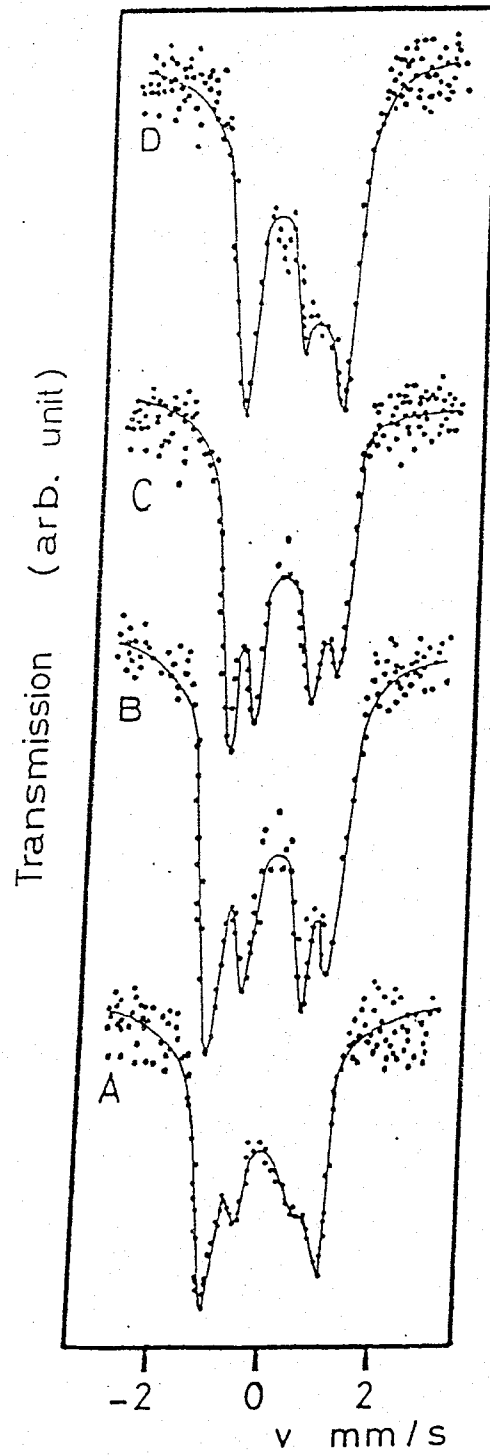


Fig. (5)  $^{57}\text{Fe}$  Mossbauer spectra for the  $\text{Y}_1\text{Ba}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7-S}$  system with  $x=0.04$  at different temperatures (A)  $200^\circ\text{K}$ , (B)  $150^\circ\text{K}$ , (C)  $100^\circ\text{K}$  and (D)  $80^\circ\text{K}$ .