

## **STUDY ON THE SUPERCONDUCTING PROPERTIES OF Mn SUBSTITUTED YBCO**

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### **ABSTRACT**

We have performed a study on the superconducting properties of  $Y_{1-x}Mn_xBa_2Cu_3O_{7-\delta}$  with various Mn doping ( $x = 0.00, 0.25, 0.30, 0.35, 0.40$  and  $0.45$ ). All of the samples displayed significant Meissner effect. XRD patterns indicate the existence of unknown peaks belonging to the impurities. A decrease in grain size as the concentration of Mn increases was observed from the SEM micrographs. The resistivity results showed the shifting in  $T_{C(R=0)}$  towards low temperature as the Mn concentration increases.

### **INTRODUCTION**

Extensive studies have been carried out on the Y-Ba-Cu-O system since the discovery of superconductivity above 90 K[1]. However, the mechanism responsible for high transition temperature in this material is still yet to be well understood. The superconducting properties of high- $T_c$  superconductors are very dependent on the structural properties as such oxygen occupancy and ordering, and density of charge carriers[2]. One of the ways to reveal the intrinsic superconducting properties is by partial substitution of one of the components of high- $T_c$  superconductors by magnetic ions[3]. This allows strong interaction between the charge carriers and localized magnetic moments that offers new possibilities for studying the impurity-environment interaction through magnetic measurements. Hence, the occupancy sites of magnetic substitutes are critical and has great effect on the overall superconducting behaviour. According to previous report,  $YBa_2Cu_3O_{7-\delta}$  is hardly affected by the substitution of Y with trivalent rare earth ions having large localized moments while  $T_c$  is decreased significantly by incorporating 3d transition metals[4]. The relative isolation of Y site from the Cu-O planes which contains metallic and superconducting electrons have been attributed for the absence of substitution effect on Y site. Conversely, doping on the Cu site creates strong effect on superconductivity and decrease  $T_c$  at various rates[5].

To date, there has been less attention paid to the Mn substitution, which is a 3d transition metals as well as other metals from the same series because of their small solubility in the structure. Mn possesses interesting magnetic properties and is known to give higher localized moment [6]. It's believed that Mn doping in YBCO compound prefers Cu1 site [7] and reduces the mobile holes and consequently results in the decrease of  $T_c$ . In addition, it is also reported that the amounts of extra phases,  $Y_2BaCuO_5$  and the tetragonal  $Ba_2Mn_3O_8$  increases with increase  $x$  [8] in  $YBa(Cu_{1-x}Mn_x)_3O_{7-\delta}$ . Although the mechanism for  $T_c$  depression is unknown, but the dependent on the occupied site (Cu1 or Cu2) by dopant is critical account as this may induce structural changes in the Y-Ba-Cu-O system. Nevertheless, some of the questions regarding the normal state properties still remain unsolved.

In this paper, we report our study on the effects of Mn substitution for Y on the superconducting and magnetic properties of Y-123 phase compound.

## EXPERIMENTAL DETAILS

Powders of  $Y_{1-x}Mn_xBa_2Cu_3O_{7-\delta}$  were prepared by employing solid state reaction method. Appropriate amounts of  $Y_2O_3$ ,  $BaCO_3$ , CuO and MnO (purity  $\geq 99.99\%$ ) were mixed and ground in a mortar and then calcined in air at  $910^\circ C$  for 48 hours with several intermittent grindings followed by furnace cooling at the rate of  $60^\circ C/h$ . The reacted powders were reground again and then pressed into pellets of  $\sim 10$  mm diameter and 3 mm in thickness. The pellets were further sintered at  $920^\circ C$  for 24 hours and slow cooled to room temperature at the rate of  $60^\circ C/h$ .

Variations of electrical resistance as a function of temperature were measured by employing the standard four point probe technique. Silver paste was used as electrical contact between the samples and probe. The phase formation in the samples was examined by X-ray powder diffraction using Phillips PW1830 diffractometer with Cu- $K_\alpha$  as radiation source. Microstructures were investigated and recorded using a JEOL 6400 scanning electron microscope (SEM). Ac susceptibility measurements were also performed using Lakeshore AC susceptometer Model 7000. The amplitudes of the ac fields varied from 0.1 Oe to 10 Oe at a fixed frequency of 125 Hz.

## RESULTS AND DISCUSSION

The magnetic levitation test revealed Meissner effect for all samples at liquid nitrogen temperature (77K). The degree of the magnetic floating is inversely proportional to the Mn concentration. The spectra of the X-ray diffraction in Figure 1 show the disappearance of (002) peak followed by the increase in the intensity of (102) peak for all the doped samples. In addition, the peaks belonging to the impurity or secondary phase appeared at  $2\theta = 31^\circ$  and  $45^\circ$ . The intensity of these peaks increased with the doping concentration. By calculating the lattice parameters, all the doped samples are preserved orthorhombic structure as the pure sample as indicated in Table 1.

The curves for temperature dependent of normalized resistance are plotted in Figure 2 which indicates the gradual decrease in  $T_{C(R=0)}$  with Mn substitution on Y from 90K ( $x = 0.00$ ) to 3K ( $x = 0.45$ ). Samples with  $x = 0.25, 0.30$  and  $0.35$  showed metallic-like behaviour while  $x = 0.4, 0.45$  showed semiconductor behaviour in the normal state. SEM micrographs of fractured surface in Figure 3 show the flaky grain of  $Y_{1-x}Mn_xBa_2Cu_3O_{7-\delta}$ . The grains of the pure sample (Figure 3a) has an average grain size of  $\sim 25 \mu m$  and some gaps and voids were also observed. However, the grain size for doped samples tend to decrease as Mn concentration increased which the average grain size found to be less than  $3 \mu m$  for the sample with  $x = 0.45$ . In addition, the shape of the grains showed a degree of irregularity and distributed randomly with no alignment in certain direction. The increment in gap and voids were clearly seen for high doping concentration and reduced the connectivity between grains. Hence, it can be concluded that there will be a decrease in  $T_{C(R=0)}$  due to the poor connectivity among grains. This is in good agreement with the results obtained from electrical resistance measurements showing that  $T_{C(R=0)}$  decreased from 88 K to 72 K as Mn concentration increased from  $x = 0.00$  to  $x = 0.45$ .

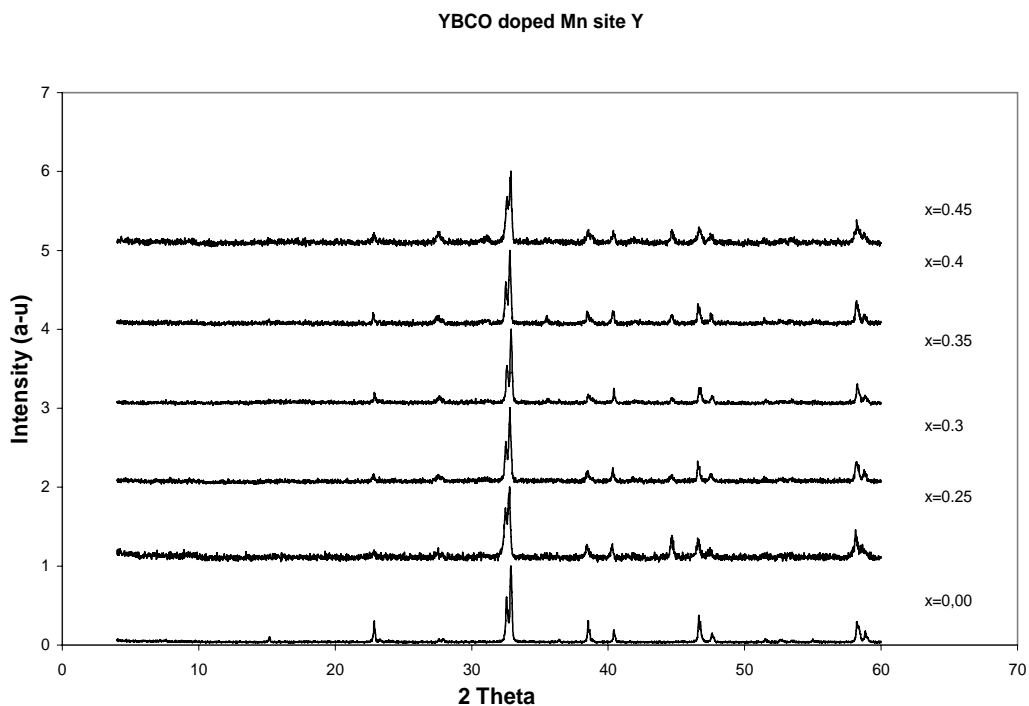


Figure 1. X-ray diffraction pattern for  $Y_{1-x}Mn_xBa_2Cu_3O_{7-\delta}$

Table 1. The lattice parameter obtained from the XRD data.

Concentration (x)	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$
0.00	3.815	3.881	11.680
0.25	3.821	3.889	11.676
0.30	3.820	3.889	11.663
0.35	3.824	3.879	11.670
0.40	3.813	3.891	11.663
0.45	3.826	3.886	11.685

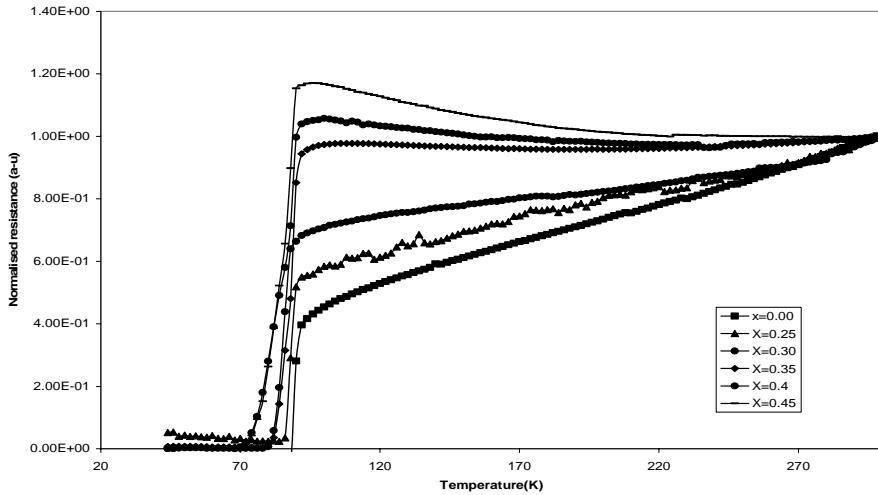


Figure 2. Temperature dependence of normalized resistance

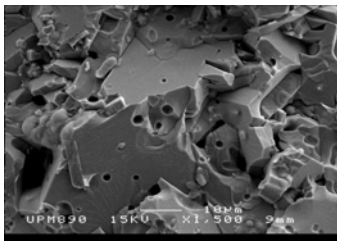
The temperature variation of the complex magnetic susceptibility,  $\chi = \chi' - i\chi''$  in various ac fields, H (0.1 – 10 Oe) for all the samples are shown in Figure 4. The real  $\chi'(T)$  and imaginary  $\chi''(T)$  parts of ac susceptibility as function of temperature were obtained at 125 Hz. The curve of real  $\chi'(T)$  part provides information on the diamagnetic behavior while the imaginary part,  $\chi''(T)$  displays the features of grain coupling in the superconductor. The peaks of the graphs show shifting of  $T_c$ -onset towards low temperature as Mn concentration increased.

The real parts ( $\chi'$ ) of the temperature dependence of ac susceptibility measurement in Figure 4 show the typical intrinsic and coupling diamagnetic shielding components and not due to low- $T_c$  phases as such phases are absent in data obtained from dc resistance measurement. The intrinsic  $T_c$ -onset for all the compositions is at 94K in accordance to the resistance versus temperature curve in Figure 2. However, the coupling temperature,  $T_{c_j}$  occurred at lower temperature in the  $\chi'(T)$  curve decreased from 94K ( $x = 0.00$ ) to 69K ( $x = 0.45$ ) as shown in Table 2. This indicates the poor coupling among grains with the increase of Mn content. For all the samples, the shoulder became broader as the magnitude of ac fields were increased from 0.1Oe to 10Oe. The broadening in the shoulder is due to the intergrain Josephson-like coupling and the shielding critical current decreased much faster than the intragrain shielding critical current as the applied fields increased.

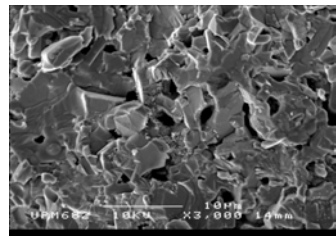
The dissipative component, ( $\chi''$ ) of the ac susceptibility for all the samples show bell-shape dependence on temperature as depicted in Figure 4. The intrinsic loss peak occurred near to  $T_c$ -onset which is due to intragranular flux pinning, was missing at lower applied fields and was not resolved until 10Oe. This shows the poor coupling among grains as evidenced from Table 2 where the Josephson current ( $I_0$ ) and the Josephson coupling energy ( $E_j$ ) decreased with increasing Mn substitution. The coupling peaks,  $T_p$ , that occurred well below the  $T_c$ -onset were observed and is field dependent. The coupling peaks which due to hysteresis loss at grain boundaries were broaden as the applied fields increased. At all applied fields,  $T_p$  decreased as the Mn content increased. Therefore, Mn doping caused greater ac loss in the samples.

Table 2. Calculated values of  $T_{c(R=0)}$ ,  $T_{cj}$ ,  $I_0$  and  $E_j$ .

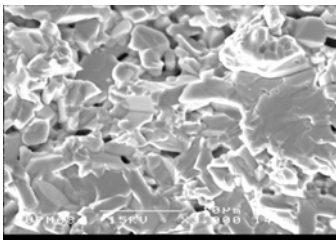
Samples ( $Y_{1-x}Mn_xBa_2Cu_3O_{7-\delta}$ )	$T_c$ (K)	$T_{cj}$ (K)	$I_0$ (maximum Josephson current, $\mu A$ )	$E_j$ (Josephson coupling energy $\times 10^{-20}J$ )
x = 0.00	90	91	46.24	1.52
x = 0.25	84	88	23.12	0.76
x = 0.30	80	83	12.61	0.42
x = 0.35	79	74	6.94	0.23
x = 0.40	73	70	5.78	0.19
x = 0.45	72	69	5.55	0.18



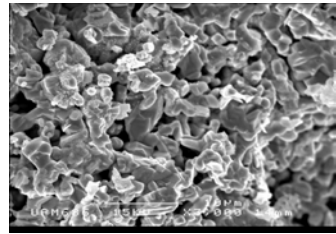
x = 0.00



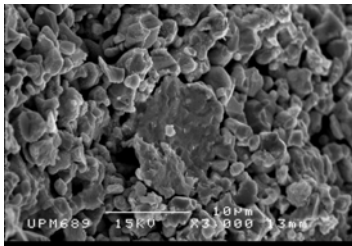
x = 0.25



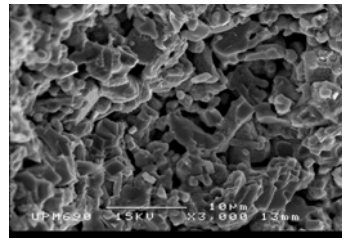
x = 0.30



x = 0.35



x = 0.40



x = 0.45

Figure 3. SEM micrographs showing the microstructures of the materials

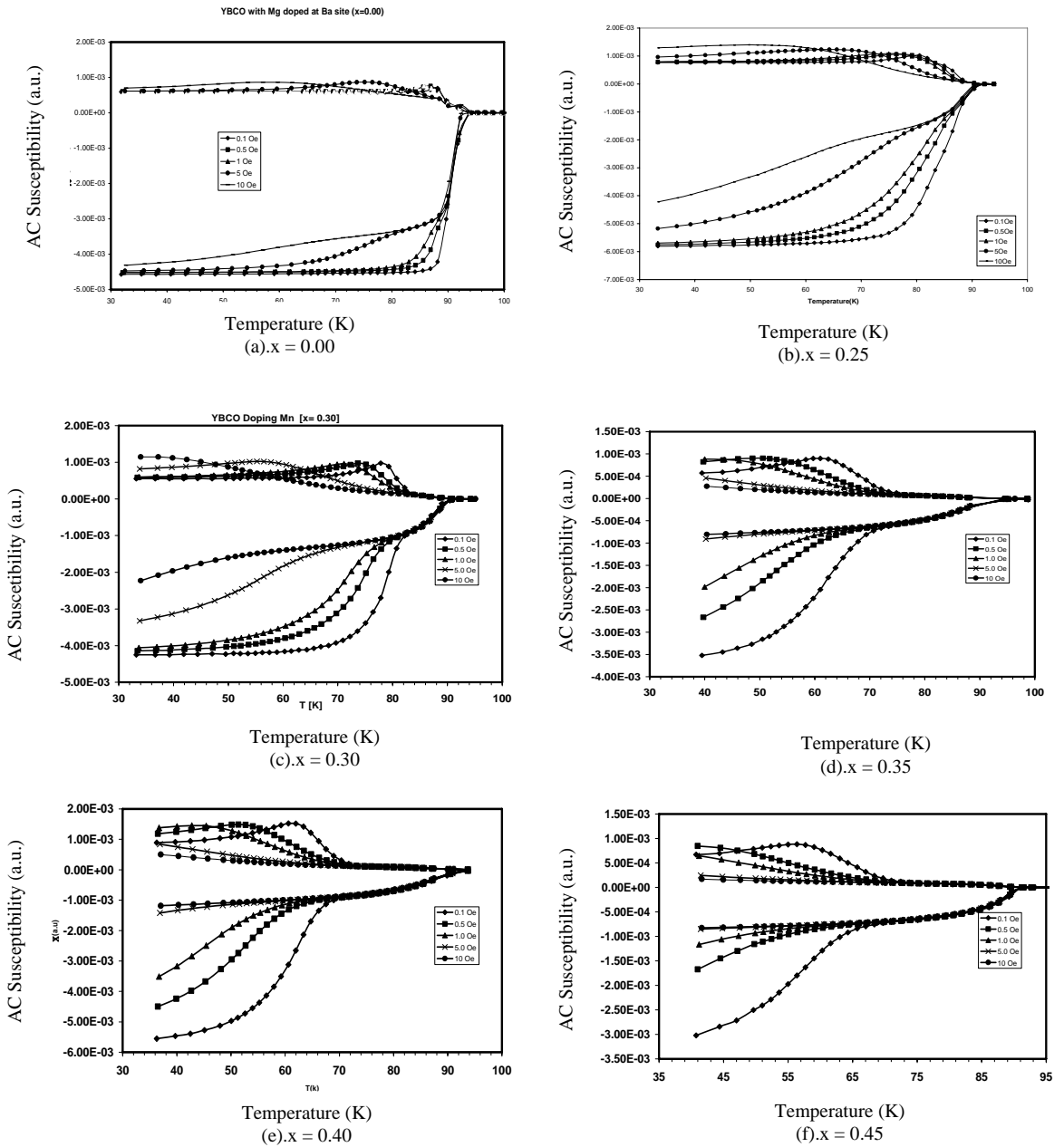


Figure 4 Ac susceptibility vs. temperature for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$  doped with Mn at Ysite

## CONCLUSION

Superconducting properties of Mn doped  $Y_{1-x}Mn_xBa_2Cu_3O_{7-\delta}$  ceramic with  $x = 0.0, 0.25, 0.30, 0.35, 0.40$  and  $0.45$  were investigated. The system displayed Meissner effect for all samples. XRD patterns showed the existence of the unknown peaks, which belong to the impurities. SEM micrographs showed the decrease in grain size as the concentration of Mn increases. The resistivity results showed the shifting in  $T_{C(R=0)}$  towards low temperature as the Mn concentration increases. In addition, ac loss is greater as Mn content increases due to the poor quality of the coupling of the grains.

## ACKNOWLEDGEMENT

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