The influence of magnetic nano metal oxides doping on structure and electrical properties of YBCO superconductor

A H Salama¹, M El-Hofy², Y S Rammah² and M Elkhatib²

¹Department of Physical Chemistry, Inorganic Chemical Industries and Mineral Resources Division, National Research Centre, 33 El Bohouth St. Dokki, Giza, P.O.12622, Egypt
²Department of Physics, Faculty of Science, Menoufia University, Shebin El-Koom, Egypt

E-mail: alia2005salama@yahoo.com

Received 11 December 2015
Accepted for publication 11 January 2016
Published 15 February 2016

Abstract
Superconductor samples of YBa₂Cu₃O₇₋δ (YBCO) + x where x = 0.1, 0.2, 0.3, 0.4 and 0.5 wt% of nano metal oxides namely Cr₂O₃, Co₃O₄ and Mn₃O₄ namely are synthesized by the solid-state reaction route. Both x-ray diffraction and electron microscopy have been employed to study the phase identification and the microstructure of these samples. Transition temperature of the samples has been determined by four probe resistivity measurements. The x-ray diffraction patterns indicate that the gross structure of YBCO does not change with the substitution of three types of nano metal oxides with different doping level. The critical transition temperature (Tc) is found to decrease with the increases of doping level. Mn₃O₄ has highest Tc value which may be due to flux pinning from some defects and the rapid suppression in Tc with increasing concentration of Mn₃O₄ may be due to the cooper pair breaking and the hole filling in the CuO₂ planes.

Keywords: YBCO superconductor, nano oxides, magnetic moment, solid state reaction, electrical property
Classification numbers: 2.01

1. Introduction

An important characteristic of the copper-oxide superconductors is the close relation between magnetism and superconductivity. Nano doping in bulk high superconducting critical transition temperature (Tc) superconductors has generated great interest because they represent easily controlled and efficient tools for improving superconducting properties. It is known that the oxygen content affects the crystal structure, electron/hole transport and superconducting properties in YBCO. It is also realized that the superconducting transition temperature sensitively depends on both the hole concentration in the CuO₂ planes and the relative concentration of the oxygen within the planes. The level of this concentration can be controlled either by manipulating the oxygen stoichiometry in the Cu-O chains, by application of pressure or by ionic substitution [1]. Elemental substitutions play an important role in understanding the nature of superconductivity in high Tc superconductors. Substitutions of Cu by X ions in RBCXO system, where R is a rare earth and X is Mn, Cr, Fe, Co, Ni, Al, and Ga, have been studied [2–12]. In the YBa₂Cu₃O₇₋δ (YBCO) system, the existence of two kinds of Cu sites (planes and chains) as well as the sensitivity of Tc to the oxidation state complicates the experimental results [13, 14].

In the first part of this work [15] we study the effect of doping YBCO with 0.2 wt% of nonmagnetic and magnetic nano metal oxides (Mn₃O₄, Co₃O₄, Cr₂O₃, CuO and SnO₂). We concluded that the doping with nonmagnetic nano metal oxides (CuO and SnO₂) severely depressed the value of Tc while doping with Cr₂O₃ (3.8 μB) and Co₃O₄ (3.2 μB)
slightly depressed $T_c$. Furthermore, doping with high magnetic moment $\text{Mn}_3\text{O}_4$ (5.27 $\mu$B) increased $T_c$ significantly which is attributed to the inclusion of Mn in YBCO structure reduced the formation of other YBCO phases and enhanced the formation of YBCO with high orthorhombicity and high superconducting properties.

In this work we investigate the effect of magnetic nano metal oxides doping to YBCO superconductor with different magnetic moments and different concentrations. The influence of this difference in magnetic moment and concentration on the microstructure and its critical temperature are studied in details.

2. Experimental details

2.1. Preparing nano metal oxides

Nano metal oxides have been prepared by the co-precipitation method [15–17]. The chemicals used were of analytical grade and used without further purification. Manganese chloride ($\text{MnCl}_2$ · $4\text{H}_2\text{O}$), cobalt chloride ($\text{CoCl}_2$ · $6\text{H}_2\text{O}$), chromium chloride ($\text{CrCl}_3$ · $6\text{H}_2\text{O}$) and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$ · $2\text{H}_2\text{O}$) with purity 99.5% are used. Oxalic acid and each metal chloride were dissolved in water separately to a concentration of 0.1 M. The aqueous metal chloride solution was put in a 100 ml burette and is allowed to drip in the flask containing the oxalic acid solution. The dripping process was completed in 30 min. After which, 5 ml ammonia solution (NH$_4$OH) was added drop by drop in the solution to increase the pH value of the prepared solution and then the two solutions interact and the corresponding metal oxalate precipitate in water. 

During precipitation the solution is subjected to magnetic stirring at the rate of 550 rpm. The resultant precipitated oxalate solution has been kept in an oven for drying over night at 90 $^\circ$C then the dried product is grinded in powder form and put in furnace at 700$^\circ$C for 5 h to obtain nano metal oxide powder except of manganese oxalate which calcinated at 1100$^\circ$C for 2 h to obtain $\text{Mn}_3\text{O}_4$ phase.

2.2. Doping YBCO with nano metal oxides

YBCO powder is prepared by the solid state reaction route by mixing stoichiometric amount of $\text{Y}_2\text{O}_3$, $\text{BaCO}_3$, CuO followed by grinding, calcinations and sintering as previously described in details in our previous work [18]. A series of polycrystalline composite samples of $\text{YBCO} + x$ where $x$ = 0.1, 0.2, 0.3, 0.4 and 0.5 wt% of each metal oxide namely $\text{Cr}_2\text{O}_3$, $\text{Mn}_3\text{O}_4$ or $\text{Co}_3\text{O}_4$ were mixed separately and pressed into pellets. The pellets were sintered according to the same curve of heat treatment as in reference [18].

XRD was done for phase conformation and structural analysis using x-ray diffractograms provided with computer controlled formally made by the PHILIPS®MPDXPERT x-ray diffratometer equipped with Cu radiation CuK$\alpha$ ($\lambda$ = 1.54056 Å). The x’pert diffractometer has the Bragg-Brentano geometry. The x-ray tube used was a copper tube operating at 40 kV and 30 mA. The scanning range (20) was 20–80$^\circ$ with step size of 0.02$^\circ$ and counting time of 3 s/step. Quartz was used as the standard material to correct for the instrumental broadening. The transmission electron microscope (TEM) images were taken for the prepared metal oxides using a JEDL model 1230. Scanning electron microscope (SEM) was used for microstructural analysis using Philips XL 30 equipped with EDX unit, accelerating voltage of 30 kV, magnification up to 400,000$\times$, and resolution for W (3.5 nm). Temperature dependent resistivity $\rho$(T) was measured using the standard four-probe techniques with a 182-Keithley nanovoltmeter and constant current source (224-Keithley), with the voltage resolution of 10–8 V of the nanovoltmeter, a constant current source of 1 mA flowing through the samples.

A closed cycle helium refrigerator consists of cryo-compressor (model 531-120-IBARA), cooled head (model CCS-100EB-JAUS RESEARCH Co.), supplied with a suitable holder, vacuum pump (model RVB-EDWARDS) and a temperature controller (321-autotuning temperature controller-LAKESKORE) having a temperature resolution of $\pm$0.1 K was used for temperature variation.
Figure 2. XRD of YBCO doped different oxides (a) Co$_3$O$_4$, (b) Mn$_3$O$_4$ and (c) Cr$_2$O$_3$ at different concentration $x$: YBCO + $x$ wt% with $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and $0.5$.

Table 1. The doped samples of YBCO with different proportions of various oxides.

| Samples of YBCO + $x$ (wt%) | $a$ (Å) | $b$ (Å) | $C$ (Å) | $V$ ($Å^3$) | $\delta = (b - a)/(b + a)$ | $O_{7-\delta}$ |
|-------------------------------|---------|---------|---------|------------|------------------------|---------------|
| YBCO                         | 3.823   | 3.885   | 11.68   | 173.4755   | 0.008 043 591          | 6.8519        |
| YBCO + 0.1 Co$_3$O$_4$        | 3.84118 | 3.88435 | 11.6883 | 174.3956   | 0.005 587 966          | 6.803 1395    |
| YBCO + 0.2 Co$_3$O$_4$        | 3.8459  | 3.8796  | 11.6894 | 174.4123   | 0.004 362 177          | 6.796 8736    |
| YBCO + 0.3 Co$_3$O$_4$        | 3.850259| 3.869809| 11.6763 | 173.9755   | 0.002 532 348          | 6.873 0602    |
| YBCO + 0.4 Co$_3$O$_4$        | 3.812788| 3.93962 | 11.6112 | 174.4124   | 0.016 360 336          | 7.254 2858    |
| YBCO + 0.5 Co$_3$O$_4$        | 3.858127| 3.880718| 11.7289 | 175.6098   | 0.002 919 169          | 6.565 0931    |
| YBCO + 0.1 Mn$_3$O$_4$        | 3.834756| 3.88479 | 11.6894 | 174.1406   | 0.006 481 469          | 6.796 4637    |
| YBCO + 0.2 Mn$_3$O$_4$        | 3.8277 | 3.8866  | 11.662  | 173.4925   | 0.007 635 171          | 6.957 328     |
| YBCO + 0.3 Mn$_3$O$_4$        | 3.8549 | 3.865079| 11.7289 | 174.7559   | 0.001 318 527          | 6.565 0931    |
| YBCO + 0.4 Mn$_3$O$_4$        | 3.823697| 3.903938| 11.6894 | 174.4943   | 0.010 383 643          | 6.796 4637    |
| YBCO + 0.5 Mn$_3$O$_4$        | 3.833687| 3.89456 | 11.6652 | 174.1873   | 0.007 876 689          | 6.930 8589    |
| YBCO + 0.1 Cr$_2$O$_3$        | 3.814336| 3.89239 | 11.6112 | 172.3915   | 0.010 128 036          | 7.254 2858    |
| YBCO + 0.2 Cr$_2$O$_3$        | 3.853  | 3.8693  | 11.7346 | 174.9443   | 0.002 110 77           | 6.532 1824    |
| YBCO + 0.3 Cr$_2$O$_3$        | 3.848597| 3.874925| 11.7346 | 174.9987   | 0.003 408 808          | 6.532 0653    |
| YBCO + 0.4 Cr$_2$O$_3$        | 3.840836| 3.87713 | 11.6847 | 174.004    | 0.004 699 931          | 6.823 8698    |
| YBCO + 0.5 Cr$_2$O$_3$        | 3.83405 | 3.887428| 11.6714 | 173.9356   | 0.006 912 925          | 6.903 8042    |
3. Results and discussion

3.1. TEM images of prepared nano metal oxides

The metal oxides of Mn$_3$O$_4$, Cr$_2$O$_3$ and Co$_3$O$_4$ are investigated by transmission electron microscope and its results are shown in figure 1. In our previous study [18], x-ray powder diffraction was done to obtain the particle size of the prepared metal oxides. The particle size is in the nano scale range (75–82 nm).

From TEM measurement, all the prepared samples are in the nano scale and show spherical shape with 75–82 nm size range in agreement with the particle size calculated from the XRD patterns of the all prepared metal oxide samples.

3.2. XRD analysis of YBCO samples

Figure 2 shows the powder x-ray diffraction patterns of the YBCO samples doped with different nano metal oxides. The analysis of the data indicates a predominantly single phase perovskite structure YBCO with orthorhombic Pmmm symmetry and small quantities of secondary phases.

The lattice parameters of YBCO with orthorhombic structure are $a_0 = 3.823$ Å, $b_0 = 3.885$ Å, $c_0 = 11.7$ Å. It should be mentioned that no peaks corresponding to any other compounds were detected by x-ray diffraction. Unit cell volumes and the lattice parameters of these samples are presented in table 1. It may be noticed that the lattice constants $a$, $b$ and $c$ changes slightly with doping with different nano metal oxides as shown from table 1. Generally, the addition of nano metal oxides slightly decrease the difference between $a$ and $b$ parameters and thus reduces the orthorhombicity ($\delta$). The high value of orthorhombicity of undoped YBCO sample is the result of a high oxygen content of the undoped YBCO sample with fully occupied O$(1)$ sites in the CuO chains along the $b$-axis as shown from the $O_{7-8}$ value which increased with nano metal oxide content indicate that the orthorhombicity of the system decreases. The low variation in the $a$-axis and changes in the unit cell volume with increasing nano metal oxide ($\text{Mn}^{2+}$, $\text{Mn}^{3+}$, $\text{Co}^{2+}$, $\text{Co}^{3+}$ and $\text{Cr}^{3+}$) doping level most probably indicate that metal ions are incorporated into crystal structure.

3.3. Microstructural study

The scanning electron microscopic (SEM) images of YBCO doped 0.2, 0.4 and 0.5 wt% of Co$_3$O$_4$, Mn$_3$O$_4$ and Cr$_2$O$_3$, samples are presented in figures 3, 4 and 5, respectively.
These pictures depict that the average grain size in all samples mostly does not change in most samples and the YBCO samples exhibits large grains randomly oriented in all directions with the presence of pores between the grains. For each doping of nano oxides, it is shown that nanodots are distributed randomly over the YBCO grains mostly. From graphs it is obvious that the grains of all samples are in the same range 1–4 μm.

The EDX analysis of 0.4 wt% Co₃O₄ and 0.5 wt% of Mn₃O₄, Cr₂O₃ samples are represented in table 2, one can note that each of Mn₃O₄ and Co₃O₄ is distributed over the entire surface of the granules as points in the nanosize range, conversely Cr₂O₃ tends to merges through the structure between or covering the YBCO grains (as shown in figures 3, 4 and 5).

3.4. Temperature dependence of resistivity

The temperature dependence of resistivity ρ(T) for doped YBCO samples with different concentrations of Co, Mn and Cr nano oxides are shown in figure 6. Generally, all samples show metallic behavior in the normal state (dρ/dT > 0) and superconducting transition to zero resistance. At higher temperature, all samples exhibited linear temperature dependence. The resistive transition exhibits two different regimes. The first is characterized by the normal state that shows a metallic behavior (above 2Tc). The normal state resistivity is found to be linear from room temperature to a certain temperature and follows Andersom and Zou relation ρ(T) = A + BT, where ρ(T) is calculated by using the values of A and B parameters which are obtained from the linear fitting of resistivity in the temperature range 2Tc to 300 K and extrapolation to 0 K gives resistivity slope (dρ/dT) and residual resistivity ρ0 as seen from figure 6. The second region is characterized by the contribution of Cooper pairs fluctuation to the conductivity below Tc, where ρ(T) is deviated from linearity. This is mainly due to the increasing rate of Cooper pair formation on decreasing the temperature. Note that doping with Co₃O₄ shows degradation of Tc from 92 to 83 with increasing the doping concentration, whereas the residual resistivity ρ0 increased with the increasing the doping concentration as seen in figure 6(a). Figure 6(b) shows that doping YBCO with different concentrations of nano Mn₃O₄ improves Tc to 119 K and 112 K at low doping ratios and then decreases Tc with increasing concentrations (0.3 and 0.4 wt%) and, finally slightly improves again at 0.5 wt% to become lower.
The residual resistivity $\rho_0$ of YBCO samples doped with Mn$_3$O$_4$ increased with the increasing the doping ratio. Figure 6(c) shows that YBCO samples doped with different concentrations of Cr$_2$O$_3$ exhibit the decay of the resistivity at $T_c$ for all doping ratios, and the value of the residual resistivity $\rho_0$ oscillates, decreasing and increasing again with the increase of doping concentration. The transition width ($\Delta T$) increases with increasing doping concentration of all the three doping nano metal oxides (Co$_3$O$_4$, Mn$_3$O$_4$ and Cr$_2$O$_3$) and this may be due to the gradual occurrence of non-superconducting additional phases and the effect of microscopic in-homogeneity.

Table 2. EDX analysis of some YBCO samples doped with different nano oxides.

| Elemental analysis | Y (wt%) | Ba (wt%) | Cu (wt%) | O (wt%) | Co (wt%) | Mn (wt%) | Cr (wt%) |
|-------------------|---------|----------|----------|---------|----------|----------|----------|
| YBCO + 0.4 wt% Co$_3$O$_4$ | 10.07 | 47.14 | 30.46 | 11.33 | 1.01 |     |     |
| YBCO + 0.5 wt% Mn$_3$O$_4$ | 9.88  | 47.95  | 30.00  | 11.63  |      | 0.55    |     |
| YBCO + 0.5 wt% Cr$_2$O$_3$ | 7.92  | 49.19  | 27.19  | 13.30  | 2.58    |        |     |

Figure 5. SEM photograph of YBCO doped (a) 0.2 wt%, (b) 0.4 wt% and (c) 0.5 wt% nano chromium oxide (Cr$_2$O$_3$).

Figure 7 represents the variation of $T_c$ of all the prepared samples as a function of concentration for each doping. One can note that $T_c$ decreases with increasing magnetic moment for all nano metal oxide doping. The decrease of $T_c$ with increasing concentration of Cr$_2$O$_3$, Co$_3$O$_4$ doping evidences substitutions in the YBCO. It was reported earlier that, the CuO$_2$ sheet in the YBCO structure is a superconducting layer (S) whereas the CuO chain layer is a non-superconducting (N) [19]. The hopping interaction between these S-N layers leads to the suppression of $T_c$ [20, 21]. Additionally, the decrease of $T_c$ with doping nominal concentration confirms that Cu atoms in YBCO crystals lattice were partially substituted. Some
Table 3. Variation of normal state and superconducting parameters in different samples.

| Samples          | \( T_{c0} \) (K) | \( T_c \) (K) | \( \Delta T \) (K) | \( \rho_0 \) (m\(\Omega\).cm) |
|------------------|------------------|--------------|------------------|-----------------|
| YBCO             | 87               | 92           | 5                | 2.18            |
| YBCO + 0.1 wt% Co\textsubscript{3}O\textsubscript{4} | 83               | 92           | 9                | 2.1             |
| YBCO + 0.2 wt% Co\textsubscript{3}O\textsubscript{4} | 71               | 81           | 10               | 3.13            |
| YBCO + 0.3 wt% Co\textsubscript{3}O\textsubscript{4} | 60               | 74           | 14               | 30              |
| YBCO + 0.4 wt% Co\textsubscript{3}O\textsubscript{4} | 43               | 60           | 17               | 27              |
| YBCO + 0.5 wt% Co\textsubscript{3}O\textsubscript{4} | 62               | 83           | 21               | 15              |
| YBCO + 0.1 wt% Mn\textsubscript{3}O\textsubscript{4} | 110              | 119          | 9                | 5.3             |
| YBCO + 0.2 wt% Mn\textsubscript{3}O\textsubscript{4} | 106              | 112          | 6                | 5.8             |
| YBCO + 0.3 wt% Mn\textsubscript{3}O\textsubscript{4} | 78               | 89           | 11               | 6.4             |
| YBCO + 0.4 wt% Mn\textsubscript{3}O\textsubscript{4} | 62               | 71           | 9                | 7.6             |
| YBCO + 0.5 wt% Mn\textsubscript{3}O\textsubscript{4} | 90               | 100          | 10               | 10              |
| YBCO + 0.1 wt% Cr\textsubscript{2}O\textsubscript{3} | 70               | 78           | 8                | 6.1             |
| YBCO + 0.2 wt% Cr\textsubscript{2}O\textsubscript{3} | 68               | 80           | 12               | 4.7             |
| YBCO + 0.3 wt% Cr\textsubscript{2}O\textsubscript{3} | 70               | 79           | 9                | 5.2             |
| YBCO + 0.4 wt% Cr\textsubscript{2}O\textsubscript{3} | 54               | 62           | 8                | 4.5             |
| YBCO + 0.5 wt% Cr\textsubscript{2}O\textsubscript{3} | 78               | 86           | 8                | 5.65            |

Figure 6. Resistivity dependences on the temperature for YBCO doped (a) 0.1, 0.2, 0.3, 0.4 and 0.5 wt% Co\textsubscript{3}O\textsubscript{4} nano oxide; (b) 0.1, 0.2, 0.3, 0.4 and 0.5 wt% Mn\textsubscript{3}O\textsubscript{4} nano oxide and (c) 0.1, 0.2, 0.3, 0.4 and 0.5 wt% Cr\textsubscript{2}O\textsubscript{3} nano oxide.
differences in $T_c$ decrease in comparison with undoped YBCO may be caused by solidification process as well as by the formation of secondary phases rich in doping. For Mn$_3$O$_4$ doping one can note that, there is the increase in transition temperature up to 0.2 wt% which may be due to the Mn inclusion which reduces the formation of other YBCO phases and enhances the formation of YBCO. However, the decrease in $T_c$ with increasing Mn content above 0.2 wt% indicates that Mn ions have been incorporated into the YBCO structure, which results in some changes of microstructure and chemical properties of Cu$_2$O planes. Moreover, the possible Cooper-pair breaking effect of magnetic ions is known to depress the transition temperature through the short range exchange scattering.

Table 3 represents the variation of normal state and superconducting parameters of all samples. It indicates that the values of $\rho_0$ depend on the type of doping. In general $\rho_0$ increases due to the doping. When the doping ratio increases, the value of $\rho_0$ for Co$_3$O$_4$-doped YBCO samples at first increases, then at 0.3 wt% it turns into a decay. Conversely, Mn$_3$O$_4$- and Cr$_2$O$_3$-doped samples show the monotone behaviour: $\rho_0$ of Mn$_3$O$_4$-doped samples increases and that of Cr$_2$O$_3$-doped ones decreases with increasing doping ratio. The increasing value of $\rho_0$ and the decreasing trend in the value of zero-resistance critical temperature ($T_c$) indicate that the connectivity between grains decreases gradually with the increasing the doping concentration of all oxides. All these effects are due to increased inhomogeneities in the intergranular regions. Point defects and chemical dopants may occupy various positions in a real crystal forming substituent or interstitial impurities.

4. Conclusion

Beside the magnetic moment, ionic charge and ionic radii are affecting the value of $T_c$ in doped YBCO samples which may be the reason behind the conflicting results for every doping with different concentrations. It was found that the doping with Cr$_2$O$_3$ (3.8 $\mu$B) and Co$_3$O$_4$ (3.02 $\mu$B) slightly depressed $T_c$. Furthermore doping with high magnetic moment Mn$_3$O$_4$ (5.27 $\mu$B) increased $T_c$ significantly which is attributed to the inclusion of Mn in the YBCO matrix reducing the formation of other YBCO phases and enhancing the formation of YBCO with high orthorhombicity and high superconducting properties. Mn$_3$O$_4$ induced nano-pinning centers which have high pinning efficiency and may be one of the main factors for improving the performance of YBCO by improving $T_c$.

References

[1] Gupta S, Yadav R S, Lalla N P, Verma G D and Das B 2010 Intergr. Ferroelectrics 116 68
[2] Jamadar T A and Ghosh A K 2009 Physica C 469 1971
[3] Babu T G N and Greaves C 1993 Physica C 207 44
[4] Skakle J M S 1998 Mater. Sci. Eng. R. 23 1
[5] Tarascon J M, Greene L H, Barboux P, McKinnon W R and Hull G W 1987 Phys. Rev. B 36 8393
[6] Mendels P, Bobroff J, Collin G, Alloul H, Gabay M, Marucco J F, Blanchard N and Grenier B 1999 Europhys. Lett. 46 678
[7] Tarascon J M, Barboux P, Miceli P F, Greene L H, Hull G W, Eibschutz M and Sunshine S A 1988 Phys. Rev. B 37 7458
[8] Xiao G, Streitz F H, Gavrin A and Chien C L 1988 J. Appl. Phys. 63 4196
[9] Xiao G, Streitz F H, Gavrin A, Du Y W and Chien C L 1987 Phys. Rev. B 35 8782
[10] Kistenmacher T J 1988 Phys. Rev. B 38 8862
[11] Goldschmidt D, Direktovitch Y, Knizhnik A and Eckstein Y 1996 Phys. Rev. B 54 13348
[12] Garcia S, Cobas R, Musa J E and Baggio-Saitovitch E M 2000 Physica C 341 1895
[13] Ishida K, Kitaoa Y, Yoshitomi T, Ogata N, Kamino T and Asayama K 1991 Physica C 179 29
[14] Pines D and Monhoux P 1995 J. Phys. Chem. Solids 56 1651
[15] Bhargava A, Alarco J A, Mackinnon I D R, Page D and Illyushechkin A 1998 Mater. Lett. 34 133
[16] El-Hofy M and Salama A 2008 Defect Diffus. Forum 280–281 1
[17] El-Hofy M and Salama A 2010 Defect Diffus. Forum 307 21
[18] Salama A H, El-Hofy M, Rammah Y S and Elkhathib M 2015 Adv. Nat. Sci.: Nanosci. Nanotechnol. 6 045013
[19] Da-Ning S and Zheng-Zhong L 1996 Physica C: Superconductivity 270 274
[20] Tang I M, Leelaprute S and Winotai P 1999 Physica C: Superconductivity 312 321
[21] Wollman D A, Van Harlingen D J, Lee W C, Ginsberg D M and Leggett A J 1993 J. Phys. Rev. Lett. 71 2134

---

Figure 7. Critical temperature $T_c$ (K) versus doping (wt%) of YBCO doped different nano oxides with different ratios.