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Structural and Electrical Properties of Niobium Doped $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_{7-y}$ Superconductors

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ABSTRACT

Polycrystalline samples of $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_{7-y}$ (YGBNCO) with different Nb contents (x = 0.05, 0.10, 0.15, 0.20, and 0.25) were prepared using the usual solid state reaction technique. The structure for all samples was characterized by XRD and SEM. The electrical properties were measured by the FPP method in the temperature range from 70 to 130 K. The lattice constant of b remains almost unchanged and a and c increases with the increase of Nb content with $x \leq$ 0.10. The zero resistance transition temperature and J_c decrease with increasing Nb content. But superconductivity did not suppress. As the Nb content in the samples increases, it gives a diffused phase indicating a niobium perovskite phase and it is a small amount of unidentified phase.

1. Introduction

YBCO is one of the most widely studied compound among the cuprate superconductors, owing to simplicity of synthesis procedure by solid-state reaction, the easy availability of the starting powders, and the non-toxity of the material compared to the other high-T_c superconductors such as Tl and Hg based oxides [1-5].

One of the most fascinating challenges of the material science is to develop $YBa_2Cu_3O_{7-x}$ (YBCO) and RE-$Ba_2Cu_3O_{7-x}$ (REBCO: RE = Er, Nd, Gd, Sm) superconductors for practical applications [6]. Several attempts have been made to study the effects of substituting Nb for YBCO [7-13]. In a study by Suresha *et al*. [14], a resistivity for $YBa_2Cu_{3-x}Nb_xO_{7-y}$ sample with x = 0.3, 0.45 and 0.6 indicated that T_c was in the range 85 - 90.3 K. They showed a possible change in crystal structure and composition with changing of x. Kuwabara and Kusaka [13] concluded that Cu and Nb did not co-exist in the same compound containing Y and Ba. Another study by Abdullah and Tan [7] mentioned that the added Nb formed perovskite YBa_2NbO_6 instead of a compound containing Cu. On the other hand, in a study by Eguchi et al. [15] it was shown that Nb substitute to Cu in the sample with nominal composition x = 0.01. Some researches [9,16] reported the existence of two phases in Y-Ba-Cu-Nb-O compound. One is the cubic Nb perovskite YBa_2-NbO_6, and the other is $YBa_2Cu_3O_y$ phase. Some previous

works indicated that at a small amount of Nb content of transition temperature, T_c, of the Y-Ba-Cu-Nb-O compound was nearly constant [9,14,17] or slowly higher [10,18].

The effect of Gd substitution in YBCO polycrystalline stabilizes an orthorhombic phase while the lattice parameters are found to increase due to a larger size of the Gd atoms than Y atoms. There is no effect in the transition temperature regardless of the concentration of Gd atoms introduced in YBCO [18], but T_c in Gd123 and Nd123 decreases rapidly with only little oxygen deficiency from fully oxygenated state, while in Y123 highest T_c is retained even with certain oxygen deficiency (up to $\delta \approx 0.2$). This may be one of the reasons why the Gd123 material is not yet considered for various applications as widely as Y123 [19]. The results of X-ray distribution maps of x = 0.4 composite indicate that the RE123 matrix is homogeneous and Y and Gd elements in the $Y_{1-x}Gd_xBa_2Cu_3O_{7-\delta}$ a perfect solid solution [20]. For the Gd diffused-doped samples, magnetization and resistivity measurements show that the critical transition temperature, T_c, increased from 88 to 91 K and the critical current density, Jc, which was calculated from M-H loops taken at 77 K, increased from 55 to 122 A·cm^{-2} in comparison with those of undoped Y123. Such enhancement, which is considered to represent a characteristic strength of inter-grain coupling, is more clearly rec-

ognized when critical current densities are compared [21].

We aimed that Nb doped to the compound which oxygen concentration is high and it is only a little affected from absence of oxygen. Because when the Nb substitutes for Cu in cuprates, Cu-O chains and CuO_2 planes are distorted, oxygen concentration reduces, thus superconductivity does not disappear. Therefore, we mixed 60% Y_2O_3 and 40% Gd_2O_3. Then we doped Nb to the $(Y_{0.6}Gd_{0.4})$ BCO compound. In **Section 2**, we gave some details about the sample preparation and experiments. Results of the dependences of the superconductivity properties and structural parameters upon the content of Nb in $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_y$ compound are summarized and discussed in **Section 3**. Some conclusions have been drawn in **Section 4**.

2. Experimental

The samples were prepared using the standard solid-state reaction technique. The detailed procedures for sample preparation were as follows: pure cation oxides of Y_2O_3 (99.995%), Gd_2O_3 (99.99%), Nb (99.8%), $BaCO_3$ (99%), and CuO (99%) were weighted and mixed according to the chemical formula of $YBa_2Cu_3O_{7-y}$ (YBCO) and $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_{7-y}$ (YGBNCO) with $x = 0.05$, 0.10, 0.15, 0.20 and 0.25, individually. Each of these mixtures was ground ten minutes for several times. They were put into a furnace (Nabartherm-N11/R) and calcined at 925°C in air at 48 h. This process was repeated two times. The calcined powders were pulverized and reground then pelletized into disk-shaped pellets. In the sintering process, the pellets were then heated up to 925°C in the tube furnace (Carbolite 201) with 10°C/min and kept at this temperature for 24 h in air. Afterwards the temperature was decreased down to about 550°C with 4°C /min and kept at this level for 12 h in flowing oxygen (≈ 2.l/min). Finally the products were cooled down to room temperature.

The structural characterization was performed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) which is equipped with an energy dispersive spectrum (EDS). A JEOL JSM-6390LV scanning electron microscope and an EDS were used. EDS analysis was carried out to displayed region with SEM for 1300 count/min. XRD experiments were carried out on Rigaku Multiflex powder diffractometer. At the XRD measurements, CuKα beam were used at $10° < 2\theta < 60°$, 5°/min scan speed and 0.02° sampling space. a, b, c, unit cell dimensions and, V, unit cell volumes were calculated from XRD data using Lapod Program which uses Cohen's method of least square. Electrical properties were measured by a standard four point probe method with silver and indium soldering contacts. The resistivity de-

pendence of temperature in the range of 70 - 130 K was measured under 10 - 6 Torr pressure with CTI-Cyro-genics Cyrodyne Refrigerator System. Critical current density of samples were measured 77 K and under 0 T external magnetic field. Jc value of samples was calculated for 2 μV/cm from I-V curves.

3. Results and Discussion

All samples were examined by powder XRD. **Figure 1(a)** and **Figure 1(b)** show the measured XRD patterns for samples (a) YBa2Cu3O7 (Y123), and (b) $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_y$ (YGBNCO) with $x = 0.05$, 0.10, 0.15, 0,20 and 0.25 respectively. The peaks of the undoped sample (YBCO) and Gd doped sample (YGBCO) were well matched to the orthorhombic Y123 structure. As can be seen there is a slight difference in the patterns for the sample with $x = 0.00$ compared to the Nb doped samples. The XRD patterns show that the peaks marked with arrow exist in the spectrum of the samples in **Figure 1(b)**. The peaks were observed at about 29.8 degrees and about 53.1 degrees and the intensity of these peaks increased gradually with the increasing of Nb content. These peaks were identified as due to niobium perovskite. With increasing Nb content samples gave a diffused phase indicating a niobium perovskite phase [22] and a small amount of unidentified phase. The results showed that the intensity of peaks owing to the YBCO decreased, while those for YBa_2NbO_6 increased with Nb content. The results of XRD analysis indicate that niobium does not go into the lattice of YBCO, but forms a secondary phase which uniformly distributes in the YBCO compound with improved microstructure. Also, there are some reports that $YBa_2Cu_{3-x}Nb_xO_y$ could be owing to the compound of this composition was not stable, leading to the formation of three components (YBCO, YBa_2NbO_6, and CuO), and Cu and Nb never coexist in the same compound containing Y and Ba [7].

Figure 2(a) and **2(b)** illustrate typical back-scattered electron SEM micrographs of the samples with x = 0.10 and 0.20. The SEM studies proved that the samples with $x \leq 0.10$ are homogeneous. The SEM micrographs show the homogeneous stone-like grains with typical size of several microns (**Figure 2(a)** and **2(b)**). The SEM micrographs show that the stone-like grains marked with A and the sponge-like grains marked with B co-exist in the surface of the samples (**Figure 2(b)**). X-ray structural analysis of the samples showed that the sponge-like grains are distributed statistically inhomogeneous. We believe that the B grains are composed of Nb impurity phase which is located on the grain boundaries and space of between the grains.

The lattice parameters (a, b and c) were calculated from ten and upper peaks using least square methods.
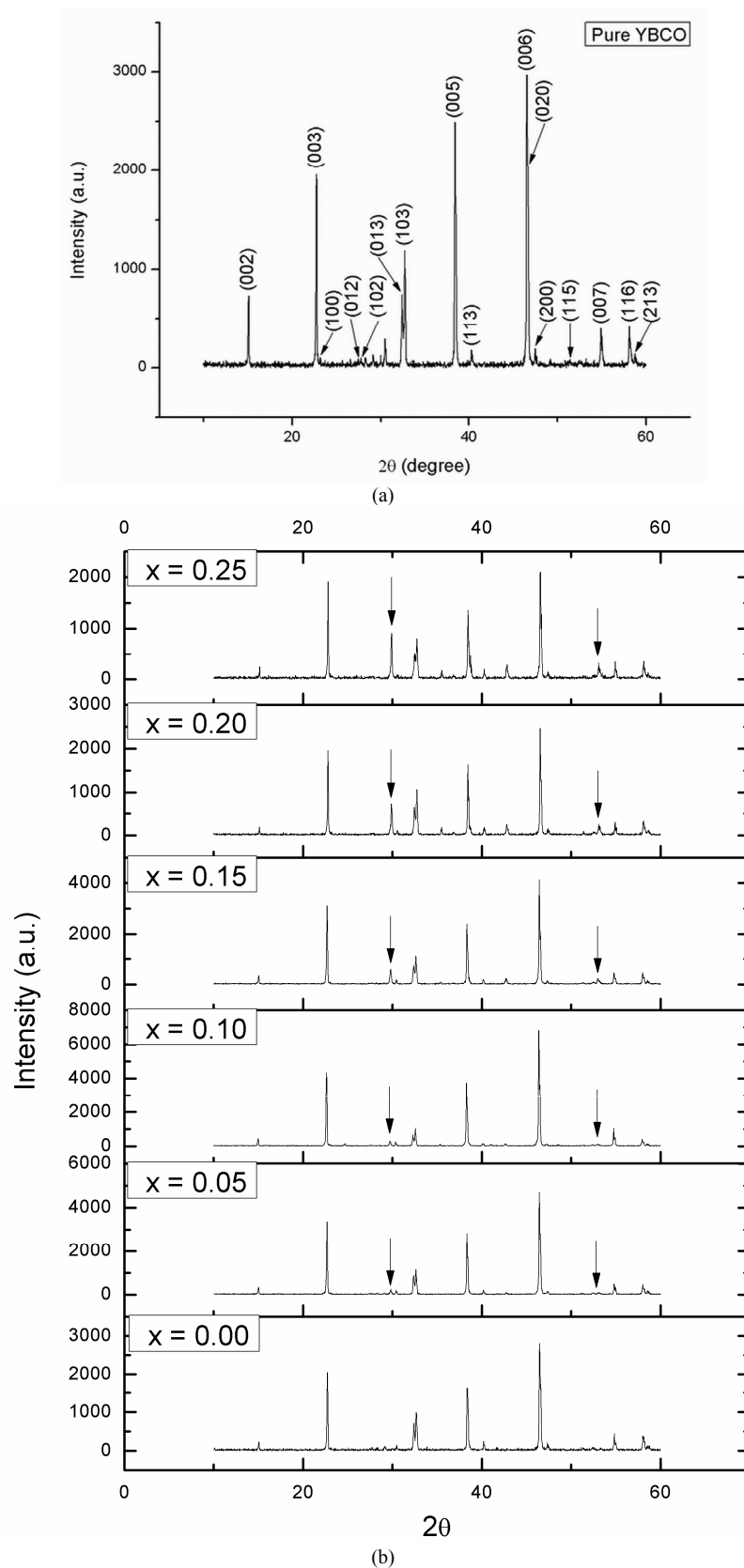
(a)

(b)

Figure 1. (a) XRD patterns for $YBa_2Cu_3O_{7-y}$; (b) XRD patterns for $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_{7-y}$.
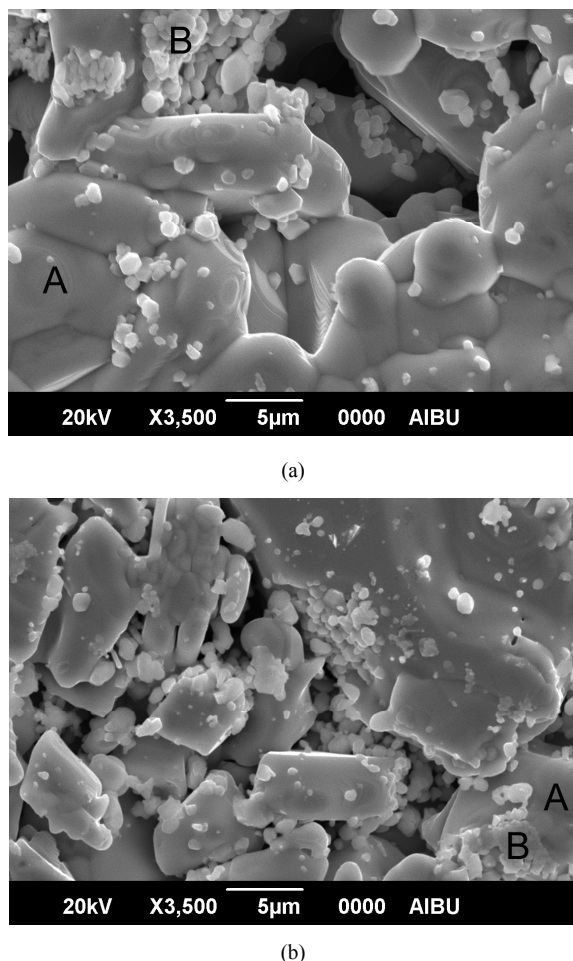
(a)

(b)

Figure 2. (a) SEM pictures of the surface structure for samples of YGBNCO with the nominal composition of *x* = 0.10; (b) SEM pictures of the surface structure for samples of YGBNCO with the nominal composition of *x* = 0.20.

The lattice parameters of a, b, c, V orthorhombicity parameters a/b and c/b are plotted in **Figure 3** versus the Nb content, *x*, for YGBNCO samples. The lattice constants of the YBCO phase for samples were found to be a = 3.829 – 3.864 Å, b = 3.887 – 3.900 Å, c = 11.692 – 11.736 Å respectively. While b lattice parameter almost remain unchanged. a and c rapidly increases with the increase of Nb content with $x \leq 0.10$ and then rapidly decreases with $x \leq 0.10$. We believe that the variations of the lattice parameters are related to the co-doping of Gd and Nb in YGBNCO.

The resistivity dependence of temperature in the range of 70 - 130 K for all samples, which are respectively normalized to that of the value of the room temperature (130 K) are shown in **Figure 4**. Good linear behavior and the metallic behavior for all samples were observed with T > 94 K. The resistivity at the normal state (T > 94 K) is measured with *x* = 0.25, bigger than with *x* = 0.05, 0.10,

0.15 and 0.20. The room temperature resistivity's increases in the doping ranges $0.00 \leq x \leq 0.25$. This result is similar to that of obtained by Strukova *et al.* [10], and can be explained that the Nb impurity phase on the grain boundaries promotes an increase in the resistivity value at room temperature.

The dependences of the zero resistance temperature, T_c^{offset}, and transition temperature, T_c^{onset}, upon the content of Nb in $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_y$ are shown in **Figure 5**, which smoothed with adjacent-averaging method versus Nb content *x*. It can be found that there is slowly increase of T_c^{onset} with the increase of Nb content (from 92 K to 95 K). This result is good agreement to compare with the other results [16-22], and can be explained as a small amount of Nb can be caused by the increase of oxygen index because of higher Nb affinity for oxygen than of Y, Ba and Cu.

All the same, it can be found that there is a slowly decrease of zero-resistance temperature, T_c^{offset}, with the increase of Nb content. T_c^{offset} almost remain unchanged as $x \leq 0.05$ (~91.5 K), and then decreases with the increase of *x* as $x \geq 0.05$. T_c^{offset} drops down to 84 K with *x* = 0.25 in **Figure 5**. The transition width, T_c, which is defined as the temperature difference between 100% and 0% in the extrapolated normal-state resistivity value (T_c^{onset} and T_c^{offset}, respectively), increases with the increase of Nb content. The larger transition width may result from the YBa_2NbO_6 phase, impurity, and unidentified phases of the sample due to the Nb doping. The impurity, YBa_2NbO_6 and unidentified phases of the samples were proved by the XRD and SEM experiments which were discussed above. Also, inhomogeneities impurity of the sample may enlarge the width of the superconducting transition, too. The oxygen content and charge transfer were believed to be an important factor for the superconductivity of YBCO.

Critical current density (Jc) values measured in the YBCO and YGBNCO for *x* = 0.00 are 89.9 and 85.9 A/cm^2, respectively. Critical current density dependence on the Nb content is shown in **Figure 6**. Jc decreases with the increase of Nb content. We think that this result is related to the YBa_2NbO_6 particles which gather between grains.

4. Conclusions

In summary, effect of Nb doped on the superconductivity properties and the structural parameters at $Y_{0.6}Gd_{0.4}Ba_{2-x}Nb_xCu_3O_{7-y}$ system with doping range ($0 \leq x \leq 0.25$) were investigated. The lattice constant of b remains almost unchanged and a and c increases with the increase of Nb content with $x \leq 0.10$. However, they decrease with the increase of Nb content, *x*, with $x \geq 0.10$. The zero resistance transition temperature and Jc decrease with increa-
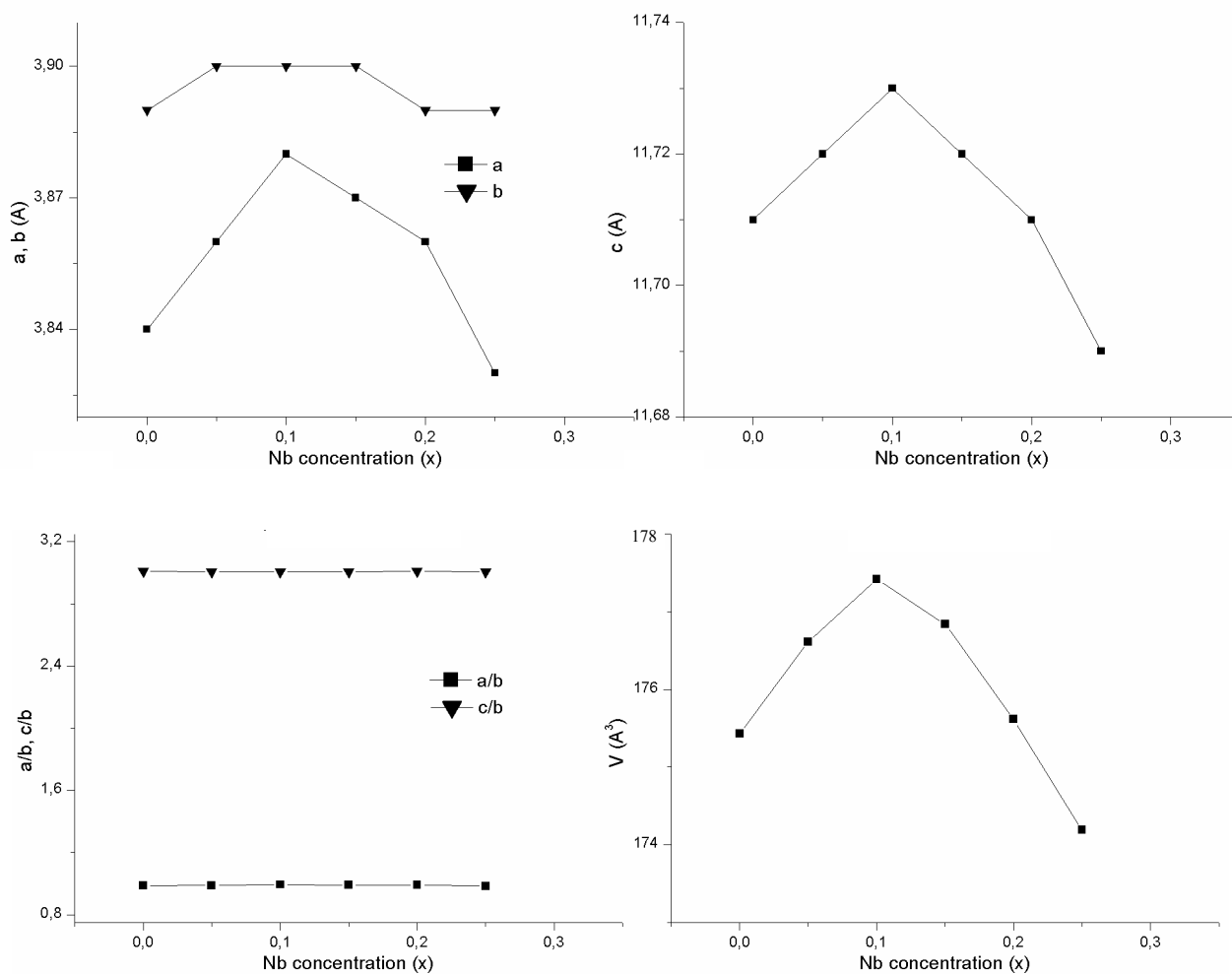
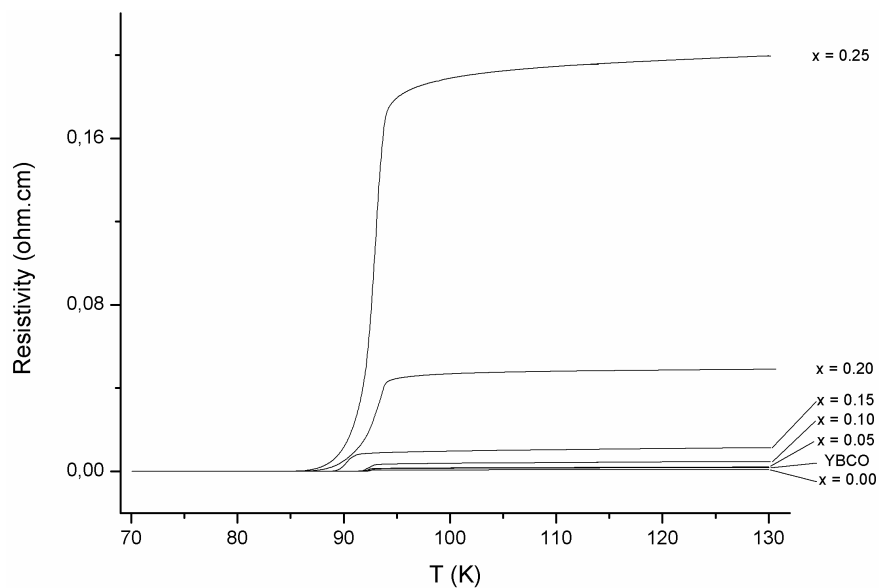**Figure 3. Lattice constants of YGBNCO versus Nb content (*x*).**

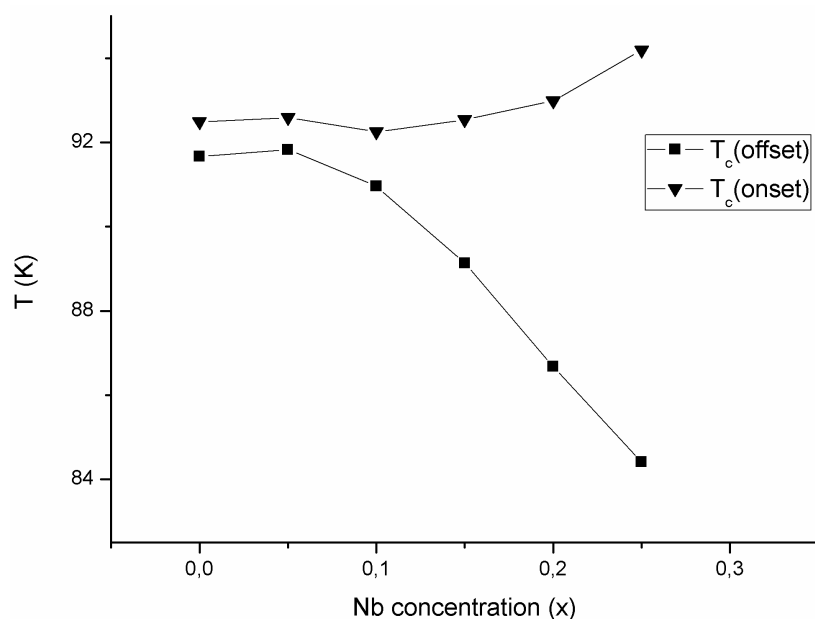**Figure 4. The temperature dependence of the normalized resistivity for YGBNCO.**

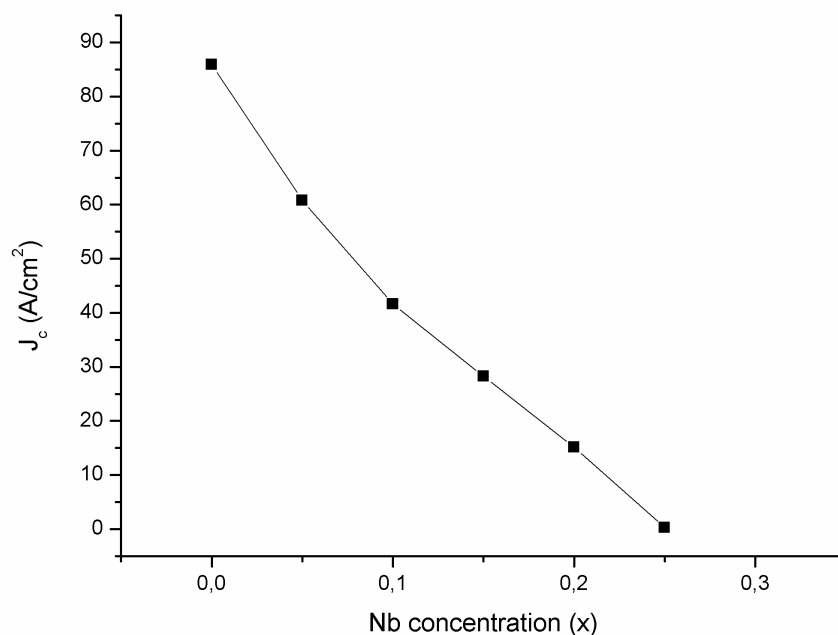**Figure 5. The T_c^{onset} and T_c^{offset} as a function of the Nb content for YGBNCO.**

Figure 6. The critical current density (J_c) as a function of the content of Nb for YGBNCO.

sing Nb content. But superconductivity did not suppress. These results show that the non-superconducting YBa_2NbO_6 particles gathered on sample surface and be-tween grains.

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