The Effects of Magnetic Dopant on the Structural and Electrical Properties in Superconducting YBaCu$_3$O$_{7-\delta}$ Ceramic

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Abstract

The work reported in this paper aims at a better understanding of the magnetic doping effects on the structural and electrical properties for a series of YBa$_2$(Cu$_{1-x}$Co$_x$)$_3$O$_{7-\delta}$ ceramics. The Co doped YBa$_2$Cu$_3$O$_{7-\delta}$ are (YBCO) prepared by conventional solid state reaction method and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), differential thermal analysis (DTA) and resistivity measurements. The crystal lattice parameters are found to change due to the cobalt doping and tendency to a structure phase transition from orthorhombic to tetragonal, which is confirmed by the decrease of the degree of orthorhombicity. The morphology examination with SEM revealed gradual increases of grain size with x = 0.02 Co, a high porosity is observed in the doped samples compared to the pure one. The decomposition temperature of YBCO is pushed from temperatures above 975°C to lower temperatures of 945°C. The resistivity measurements of doped samples with x = 0.04 and 0.06; shows a deviation in from $T$-linear behavior due to the opening of a pseudogap.

Keywords

YBCO Doped Co, Electrical Properties, Phase Transition, High Tc Superconductivity

1. Introduction

High-$T_c$ superconductors (SC) cuprates remain one of the most intriguing and not completely understood systems, however, the researchers focused on the experimental side wondering to identify new phenomena in this type of material. YBCO is one of the most widely studied compounds among the high-$T_c$, SC cu-
prates, due to simplicity of synthesis procedure by solid-state reaction, the easy availability of the starting powders, and the non-toxicity of the material compared to the other high-Tc superconductors such as Tl and Hg based oxides [1]. The partial substitution in the parent YBCO structure has been investigated intensively in an attempt to clarify or improve the superconducting behavior of this type of superconductors [2] [3] [4] [5] [6]. Transition metal oxide materials with perovskite-like structures have been extensively investigated in the recent decades for their novel properties such as superconductivity, ferroelectricity, and colossal magnetoresistance [7]. The Cu atoms in YBCO are located at two different sites in the unit cell. One of the Cu sites is in CuO₄ in the basal plane Cu(1) which forms the Cu-O chains; the other one is called Cu(2), in pyramids slightly displaced from the basal plane and forms Cu-O planes. The CuO₂ plane is sometimes referred to as the superconducting plane. Any modification in this plane strongly influences the electronic structure and the density and mobility of the charge carriers. On the other hand, the substitution at the Cu(1) chain site leads to the localization of carriers and weakening of the Cu-O chains as carrier reservoir. As a result, the hole carriers cannot easily transfer to the CuO₂ planes. The pairing and transportation of carriers are thus affected indirectly, and the superconductivity gets suppressed albeit slowly [8]. It has been reported that Co atom preferentially occupy Cu(1) [9]. While Liu et al [10] confirm that the Co atoms locate primarily at the Cu(1) sites at low doping level; upon increasing the Co concentration, some of the Cu(2) sites become occupied. YBa₂(Cu₁−ₓCoₓ)₃O₇−δ has been widely investigated as a normal layer in superconductor-normal-superconductor (SNS) Josephson junctions [11].

As a contribution in this field of research the present paper deals with the study of the effect of doping with low content of cobalt, on structural and electrical properties of YBa₂Cu₃O₇−δ ceramic.

2. Experimental

The composition YBa₂(Cu₁−ₓCoₓ)₃O₇−δ with x = 0%, 2%, 4% and 6%, were prepared by solid state reaction. The oxides Y₂O₃, CuO, and CoO, carbonate BaCO₃ (with a purity of 99.9%), were ground for 1 h and heated to 940°C for 24 h in air. The calcined mixtures were dry-ground for 1 h pelletised to 13 mm diameter disks with 2 to 3 mm thick, with pressure 2 tonn/cm² and heated to 940°C for 24 h in air. In the present paper we study the impact of the substitution of Co²⁺ impurity on the transport properties of YBCO superconductor. The crystalline structures of our samples were identified by X-ray diffraction (XRD). We have measured the resistivity of several Co substituted YBCO samples as a function of temperature, by the standard four-probe technique, for studying the modifications of the transport properties. SETARAM92 differential thermal analyser (DTA) was employed to study how the mixed powders react to investigate the sinterability of the powders mixtures, the samples were heated to 980°C in air then the samples were cooling to room temperature a rate of it approximately of
5°C/min. The grain morphology of the samples was analyzed by scanning electron microscope (model JSM-6480 LV, make JEOL).

3. Results

3.1. XRD Characterization

The structural analysis of all samples has been done by using X-ray diffraction (XRD) peaks. The XRD patterns have been shown in Figure 1. The undoped sample shows all peaks corresponding to the orthorhombic phase. They are attributed to YBa2Cu3O7−δ phase as compared to JCPDS 82-2471 file. Appearance of peaks (003), (004), (005) and (006) in the XRD pattern with high intensity compared to other peaks, reveal the presence of certain degree of (00l) orientation of YBCO. This is may be due to stress induced by thermal cycle, or to the pelletization procedure of powders. The diffraction lines of doped samples, with x = 2%; 0.04% and 6% Co, are shifted to higher 2θ values which may be due to the stress of first order. The peak intensities for YBCO structure are affected by Co doping, where the intensities of the planes are larger for the pure sample as compared with the doped samples, but as the content of Cobalt is further increased from x= 2% to 6% the intensities of (00l) peaks began to increase together.
with the disappearance of peaks corresponding to nonsuperconducting phase such as BaCuO$_2$ (011). The XRD analysis allows to confirm that no impurity phase containing Cobalt is detected in any sample which confirm that the solubility limit is higher that 6 at.% of Cobalt. As is well known, the full width at half maximum (FWHM) reflects the crystalline quality of the studied samples. The Figure 2 shows the variation of full width half maximum (FWHM) (00$l$) peaks as function of Co content. The FWHMs of doped samples are found greater than the pure one. This indicates the existence of defaults in the (00$l$) direction [12], and confirms that the grain size of the doped sample is larger than the pure one.

The Lattice parameters $a$, $b$ and $c$, and the cell volume $V$, obtained from X-ray diffraction of YBa$_2$(Cu$_{1-x}$Co$_x$)$_3$O$_{7-δ}$ are plotted in Figure 2 as function of Cobalt content $x$. The $b$ and $c$ parameters are found to decrease continuously while the $a$ parameter increases with increasing $x$. The unit cell volume decreases sharply with the increase of Co content. The decreasing of $c$ parameter confirms the shift of the lines to higher $2θ$ values as obtained in XRD patterns. The contraction of the crystallographic $c$ axis as suggested in [13] [14] could be attributed to the difference in the size of the Co$^{2+}$ and Cu$^{2+}$ ions ($r_{Co^{2+}} = 0.65$ Å and $r_{Cu^{2+}} = 0.73$ Å) [15], to the loss of oxygen which is known to affect the $c$ parameter [16] and can be linked to the reduction in the local Jahn-Teller distortion of the oxygen octahedron around Cu$^{2+}$. In cuprate oxides, the Jahn-Teller mode mainly corresponds to an orthorhombic distortion of CuO$_2$ square in which two Cu-O bonds are elongated and other two shortened [17].

The orthorhombicity $(b - a)/(b + a)$ seems to be dependent of the Co concentration (Figure 3), because it decreases with $x$. There are tendency to orthorhombic/tetragonal transition (O/T) for $x > 0.06$, it has found that this transition was observed when $x > 0.03$ for S. Elizabeth et al [18], and between $x = 0.12 - 0.15$ for Liu et al [10].
3.2. Surface Microstructure

Figure 4 shows the SEM micrographs of YBCO samples doped with 0%, 2% and 4% Co. The microstructure of those samples exhibits a granular structure with a dominant YBCO phase. It shows that pristine YBCO sample exhibits elongated grains randomly oriented in all directions with size varying from 5 to 20 μm in length. It can be seen that microstructure of the doped sample with x = 2% Co, presents an identical granular structure; but with a big grain size, compared to the case of undoped sample. The micrograph of YBCO sample doped with 4% Co shows the presence of a higher porosity and very small grain sizes. Also, it is easy to observe bright grains that the amount decreases with Co content. It is suggested that these grains correspond to the presence of the nonsuperconducting BaCuO₂ (011) phase, this result is in agreement with that obtained by XRD analysis, and other reported in [19] [20].

3.3. DTA Analysis

Figure 5 shows the DTA curves of the mixed powders. It can be seen that two endothermic peaks are observed in the DTA traces of the powders during heating. For undoped mixed powders, at about 823°C and 975°C, resulting from decomposition of BaCO₃ and partial melting of YBa₂Cu₃O₇₋δ respectively, as reported earlier [21]. In the thermograms of mixed starting powders corresponding to Co doped samples with x = 0.02, 0.04, the endothermic peaks unregistered at higher temperature are found to shift to lower values of temperature. Indeed, a shift of approximately 30°C is noted for the sample corresponding to x = 0.02 Co, 24°C for the sample with x = 0.04 Co. The peak corresponding to the decomposition of BaCO₃ seems to shift to higher values of temperature with 3°C
Figure 4. Micrographs of YBCO samples doped with: (a) 0% (b) 2% and (c) 4% Co.

Figure 5. DTA traces for Co doped YBa$_2$(Cu$_{1-x}$Co$_x$)$_3$O$_{7-δ}$ samples.}

for 0.02 Co and 2°C for 0.04 Co. This effect is also observed in the YBCO (Ag) system and YBCO(Zn) [22].

3.4. Electrical Resistivity

Measurements of different samples with various amounts of Cobalt are shown in Figure 6. As it can be seen from this figure, the resistivity of YBa$_2$(Cu$_{1-x}$Co$_x$)$_3$O$_{7-δ}$ samples vs. temperature shows that for the onset transition temperature is $T_c^{onset}$ ~ 88 K, 82 K, 81 K and 80 K for x = 0, 0.002, 0.004 and 0.006 Co respectively. Decrease in the number of hole carriers by impurity doping to the CuO chain should be responsible for reduced Tc of YBCO phase Cobalt doping, this reduction has been estimated to 2 - 8 K/at% for trivalent dopants (M: Fe, Co and Al) [23]. All samples show metallic behavior in the normal state, with high resistivity comparing to undoped sample. The residual resistivity ($\rho_0$) is found by linear extrapolation of the resistivity curve in the range from 2Tc up to room temperature.
As an inherent property of conducting materials, $\rho_0$ is modified progressively with the added composites (Figure 7). This signifies that intergranular connectivity is also modified by these composites. The residual resistivity is considered as an indicator of the sample homogeneity and defects density. The higher residual resistivity value corresponding to the sample doped with $x = 0.06$, these results are confirmed by the porous structure obtained in the micrographs analysis. Co doping makes the temperature dependence of the resistivity $\rho(T)$ deviate from linear behavior at $T_c$, especially for the sample doped with $x = 0.04$.
and \( x = 0.06 \). This deviation is related to the opening of a pseudogap. As discussed for oxygen depleting crystals [24].

4. Conclusion

The effect of Cobalt doping on the microstructure and the normal state transport properties of polycrystalline YBCO was studied. Samples have been elaborated by the solid state reaction method and characterized by means of XRD, SEM, DTA and resistivity measurements. The crystal lattice parameters are found to change due to the cobalt doping and tendency to a structure phase transition from orthorhombic to tetragonal, which is confirmed by the decrease of the degree of orthorhombicity \((b - a)/(b + a)\). The variation of full width half maximum (FWHM) of (00l) peaks as function of Co content reveals that there is a microstructural disorder caused by the cobalt incorporation. The thermal analysis of our samples reveals that the YBCO decomposition temperature is greatly lowered. In addition, the morphology examination with SEM revealed gradual increases of grain size with \( x = 0.02 \) Co; a high porosity is observed in the doped samples compared to the undoped. The resistivity measurements show a deviation from linearity of \( \rho(T) \), it is due to the opening of a pseudogap in Co doped samples.

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