Journal of Alloys and Compounds 507 (2010) 142–145

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Suppression of T_c in Co-doped $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ superconductor

Nawazish A. Khan [a], M. Mumtaz [a,b,*], Anayat Ullah [a], Najmul Hassan [c], A.A. Khurram [d]

[a] Materials Science Laboratory, Department of Physics, Quaid-i-Azam University, Islamabad 45320, Pakistan
[b] Department of Physics, International Islamic University (IIU), Islamabad 45320, Pakistan
[c] Department of Physics, Hazara University, Mansehra, NWFP, Pakistan
[d] Experimental Physics Labs, National Center for Physics (NCP), Quaid-i-Azam University, Islamabad 45320, Pakistan

ARTICLE INFO

Article history:
Received 16 February 2010
Received in revised form 18 July 2010
Accepted 20 July 2010
Available online 29 July 2010

PACS:
74.76.−w, 74.76.Bz, 74.72.−h, 74.72.−Jt

Keywords:
$(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$
superconductor
Doping
T_c suppression
Carriers localization

ABSTRACT

The most possible sources of suppression of superconducting properties (i.e., zero resistivity $T_c(R=0)$, magnitude of diamagnetism, etc.) in cobalt-doped $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ ($x=0$, 0.05, 0.1, 0.5) superconductor have been explored. It has been observed from these studies that Co-doping at Cu^{2+} sites in the CuO_2 planes somehow localizes the carriers at Co^{3+} sites and decreases the density of mobile carriers in the superconducting CuO_2 planes. We doped Li at Tl sites in $Cu_{0.5}Tl_{0.5}Ba_2O_{4-\delta}$ charge reservoir to obtain an efficient carriers doping $(Cu_{0.5}Tl_{0.25}Li_{0.25})Ba_2O_{4-\delta}$ charge reservoir layer of $(Cu_{0.5}Tl_{0.25}Li_{0.25})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ compound to replenish the density of mobile carriers in the CuO_2 planes; since alkali metals are known to lose their outermost "s-orbital" electron easily, which can be supplied to the superconducting CuO_2 planes. The increased free carrier density in the superconducting CuO_2 planes enhances the superconducting properties of the final compound.

1. Introduction

Since the discovery of oxide superconductors the exact mechanism of superconductivity at microscopic level has not been completely explored yet. In cuprate high temperature superconductors (HTSCs) $MBa_2Ca_{n-1}Cu_nO_{2n+4-\delta}$ [$n=2$–5 and M = Y, Tl, Hg, Bi, Cu, (Cu,Tl)] superconductor families, the two major constituents of unit cell are $MBa_2O_{4-\delta}$ a charge reservoir layer and $nCuO_2$ conducting planes [1]. The key structural unit in the oxide superconductors is the conducting CuO_2 planes, which is considered to be responsible for the superconductivity [2–5]. The charge reservoir layer supplies carriers to the conducting $nCuO_2$ planes and these carriers in CuO_2 planes become the source of superconductivity. The carriers in CuO_2 planes can be perturbed by directly doping at the planner sites. Many research groups working in the field of high T_c superconductivity focus their attention on the CuO_2 planes; they substitute different elements such as Co, Ni, Fe and Zn at Cu sites in CuO_2 planes in order to study the response of the superconductor material to a disorder created by these ions in CuO_2 planes [6–14]. In these studies, it was found that doping of such impurities leads to a decrease in the critical temperature "T_c". The proposed reasons for the T_c suppression after the substitution of impurity atoms in CuO_2 planes are magnetic pair breaking, potential scattering of carriers, localization of carriers and suppression of effective pairing interaction [15–17]. The magnetic ions Co, Ni and Fe produce the magnetic pair breaking and localization of carriers due the interaction between the Cooper pairs and the magnetic spins of the impurity atoms [18–20]. The $Cu_{1-x}Tl_xBa_2Ca_2Cu_3O_{10-\delta}$ ($x=0.4$–0.8) superconductor is a promising material in cuprate family of superconductors due to its low anisotropy and the ability of carrying high critical current [21,22]. In this article, we substituted Co at Cu in CuO_2 planar sites in $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_3O_{10-\delta}$ superconductor to observe the response of these materials to the substitution of magnetic impurity in CuO_2 planes. This material has Tl^{3+}/Cu^{2+} atoms in the charge reservoir layer; therefore, the charge transfer mechanism to CuO_2 planes is different from that of other cuprates, which has only trivalent atoms in their charge reservoir layer [23–25]. Therefore, we expected some different results as compared to the other superconductor materials after Co-doping. However, our experiments on Co-doped $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ superconductors have suggested that the mobile free carriers are most likely to be localized at Co^{3+} sites in CuO_2 planes due to (3+) oxidation state of cobalt [26]. These studies have also suggested that if we replenish the free carriers by some other means to CuO_2 planes, superconduc-

* Corresponding author at: Department of Physics, International Islamic University (IIU), Islamabad 45320, Pakistan. Tel.: +92 52 9019714/92 51 90642091; fax: +92 51 92102056.
E-mail addresses: mmumtaz75@yahoo.com, mmumtaz@iiu.edu.pk (M. Mumtaz).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.07.141

Table 1
Fraction of different phases present in the $Cu_{0.5}Tl_{0.5}Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ ($x = 0, 0.05, 0.1, 0.5$) superconductor.

Sr. no.	Co-concentration	% of 1223	% of 1234	% of 1212	a-axis (Å)	c-axis (Å)
1	0	95	4	1	3.98	15.02
2	0.05	94	4	2	4.03	15.08
3	0.1	94	5	1	4.04	15.32
4	0.5	95	4	1	3.89	15.88

tivity can be restored in Co-doped $Cu_{0.5}Tl_{0.5}Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ material. Therefore, we have also substituted Li at Tl sites in the $(Cu_{0.5}Tl_{0.5})Ba_2O_{4-\delta}$ charge reservoir layer to obtain an efficient carriers doping $(Cu_{0.5}Tl_{0.25}Li_{0.25})Ba_2O_{4-\delta}$ charge reservoir layer of $(Cu_{0.5}Tl_{0.25}Li_{0.25})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ compound. The objective of Li-doping was to supply required number of mobile carriers to CuO_2 planes, which would have been depleted due to the localization of carriers at Co^{3+} in CuO_2 planes; the supply of excess carriers could restore the superconductivity in Co-doped samples [27,28].

2. Experimental

The samples were prepared by solid-state reaction method accomplished in two steps. In the first step $Cu_{0.5}Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ ($x = 0, 0.05, 0.1, 0.5$) and $(Cu_{0.5}Li_{0.25})Ba_2Ca_2Cu_{2.5}Co_{0.5}O_{10-\delta}$ precursor materials were synthesized by using $Ba(NO_3)_2$, $CaCO_3$, Cu(CN), $Co(NO_3)_3$ and LiCl as starting compounds. These compounds were mixed in appropriate ratios and ground for about an hour in an agate mortar and pestle. The ground material was loaded in quartz boat and fired in chamber furnace at 850 °C for 24 h followed by furnace cooling to room temperature. The precursor material was then mixed with Tl_2O_3 and ground for about an hour. Thallium mixed material was then palletized under 3.2 tonnes/cm^2 pressure and the pellets were wrapped in a gold capsule. Pellet containing gold capsule was heat-treated at 850 °C for 10 min and quenched to room temperature to get $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ ($x = 0, 0.05, 0.1, 0.5$) and $(Cu_{0.5}Tl_{0.25}Li_{0.25})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ as final reactants compositions. The resistivity of these samples was measured by four probe method and ac-susceptibility by using SR530 Lock-in Amplifier at a frequency of 270 Hz with $H_{AC} = 5.69$ mOe of primary coil at various temperatures. The bar shaped samples of dimension 2 mm × 10 mm × 2.5 mm were used for resistivity and ac-susceptibility measurements. The structure of material was determined by using X-ray diffraction scan (D/Max IIIC Rigaku) with a CuKα source of wavelength 1.54056 Å and cell parameters were determined with the help computer software program (i.e., Check cell).

3. Results and discussion

The X-ray diffraction (XRD) scans of $Cu_{0.5}Tl_{0.5}Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ ($x = 0, 0.05, 0.1, 0.5$) {CuTl-1223} samples prepared at 850 °C are shown in Fig. 1. Most of the diffraction lines are indexed according to tetragonal structure following $P4/mmm$ space group. The inclusions of derivative phases such as Cu–Tl–Ba–Ca–Cu–Co–$O_{12-\delta}$ {CuTl-1234} and Cu–Tl–Ba–Ca–Cu–Co–$O_{8-\delta}$ {CuTl-1212} were also observed in the XRD scans. The relative percentages of these phases with Co-doping concentrations are given in Table 1, which were calculated by using the following relations [29].

% of CuTl-1223 phase

$$= \frac{\sum I(\text{CuTl-1223})}{\sum I(\text{CuTl-1223}) + \sum I(\text{CuTl-1234}) + \sum I(\text{CuTl-1212})} \times 100$$

% of CuTl-1234 phase

$$= \frac{\sum I(\text{CuTl-1234})}{\sum I(\text{CuTl-1223}) + \sum I(\text{CuTl-1234}) + \sum I(\text{CuTl-1212})} \times 100$$

% of CuTl-1212 phase

$$= \frac{\sum I(\text{CuTl-1212})}{\sum I(\text{CuTl-1223}) + \sum I(\text{CuTl-1234}) + \sum I(\text{CuTl-1212})} \times 100$$

'I' is the intensity of the phases present in the final compound.

The lengths of 'a'- and 'c'-axes increase with the increase in Co-doping at Cu sites in CuO_2 planes. The dominant phase in all these samples is CuTl-1223, while the other phases in minute quantity are due to the impurities arising during the preparation processes of these samples [10]. Some additional phases such as CuTl-1234 and CuTl-1212 are observed along with the desired CuTl-1223 phase. We have taken XRD spectra with a very slow scan speed of 1°/min to observe even small amount of impurities.

The resistivity measurements of Co-doped $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ ($x = 0, 0.05, 0.1, 0.5$) samples with magnetic ac-susceptibility measurements in inset are shown in Fig. 2. A metallic variation of resistivity from room temperature down to onset of the superconductivity is the salient feature of these samples. The zero resistivity critical temperature $\{T_c(R = 0)\}$ is observed around 114, 104, 84 and 80 K for Co-doping concentration of $x = 0, 0.05, 0.1, 0.5$, respectively. The increased concentration of Co ($x \geq 0.5$) shifts the transition temperature below 77 K. The magnetic ac-susceptibility curves of these samples

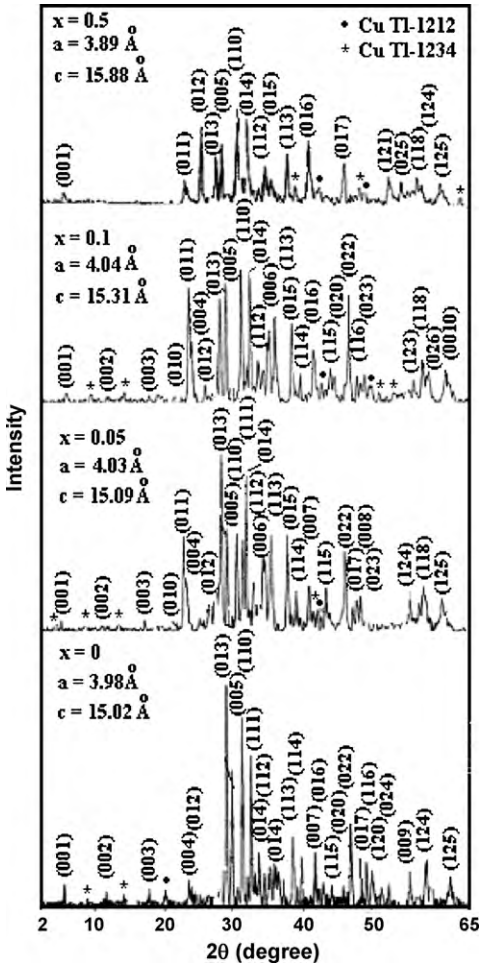

Fig. 1. The X-ray diffraction (XRD) scans of $(Cu_{0.5}Tl_{0.5})Ba_2Ca_2Cu_{3-x}Co_xO_{10-\delta}$ ($x = 0, 0.05, 0.1, 0.5$) superconductors and "*" & "·" denote the CuTl-1234 and CuTl-1212 phases, respectively.