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Superconducting properties of Cd doped $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Cd_yO_{12-\delta}$ (*y* = 0, 0.25, 0.5, 0.75, 1.0) superconductors

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A R T I C L E I N F O

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ABSTRACT

Cadmium doped $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Cd_yO_{12-\delta}$ (y=0, 0.25, 0.5, 0.75, 1.0) samples have been synthesized and their superconducting properties are studied using X-ray diffraction (XRD), resistivity, ac-susceptibility and Fourier Transform Infrared (FTIR) absorption measurements. These samples have shown tetragonal structure, their unit cell volume is decreased with the increased Cd doping. The zero resistivity critical temperature $[T_c(R=0)]$ decreases and the magnitude of diamagnetism is suppressed with the increased concentration of Cd in superconductors. The $T_c(R=0)$ and the magnitude of diamagnetism in these compounds are improved after post-annealing in oxygen atmosphere. It is most likely that the increased concentration of oxygen in $Cu_{0.5}Tl_{0.5}Ba_2O_{4-\delta}$ charge reservoir layer optimizes the density of carriers in the conducting planes to the desired level consequently increasing superconductivity in the final compound. Changes in the shape of FTIR absorption spectra after Cd doping have shown incorporation of Cd in the unit cell of the final compounds. The FTIR absorption measurements of these samples have shown hardening of apical oxygen modes of type $Cu(1)-O_A-Cu(2)/Cd_y$ (y = 0, 0.25, 0.5, 0.75, 1.0) with increased Cd doping. It is most likely that hardening of apical oxygen modes of vibration are associated with the damped harmonic oscillations of heavier Cd atoms in the CuO₂ planes which suppress the phonons population from a desired level reducing the magnitude of superconductivity in the final compound.

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1. Introduction

The substitution of impurity atoms in the high T_c cuprate (HTSC) have long been a subject of hot discussion [1,2,3] which is of immense importance in the understanding of mechanism of superconductivity. In this context the doping of non-magnetic impurity such as Zn^{2+} at the CuO₂ planner sites have been of significant importance [4]. Since the zinc atoms in their ground state have filled 3d¹⁰ shells, therefore, their presence in the CuO₂ planes would not contribute any magnetic moment to the planar lattice having two-dimensional anti-ferromagnetic aligned arrangements of Cu atoms. This would suppress the magnitude of anti-ferromagnetic aligned moments and would decrease the spin lattice scattering. In the previous studies the magnitude of superconductivity was decreased in $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ (La-214) system with the substitution of zinc and it was proposed that Zn atoms pin the spin lattice which induce the localization of carriers in the neighborhood of Zn atoms [5,6]. In YBa₂Cu_{3-x}Zn_xO_{7- δ} system it was suggested that not only the Zn atoms have large scattering cross-section but also when doped at Cu(2) planar sites liberate electrons more eas-

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ily which can deplete holes in the CuO₂ planes [7,8]. The affinity of Zn atoms to easily supply the electrons was also evidenced in filling of pseudo gap in under-doped YBa₂Cu₃O_{6+δ} superconductors [8]. In $Bi_2Sr_2Cu_{1-x}Zn_xO_{6+\delta}$ system the decreased super fluid density of the carriers in CuO₂ planes and local moments induced by Zn were found to play a key role in the reduction of critical temperature [9,10]. The $T_c(R=0)$ in HgBa₂Cu_{1-x}Zn_xO_{4- δ} system was also found to decrease with increased Zn doping, however, no Zn induced pinning of the stripes was observed [11]. In a study Panagopoulos had found that the inter-plane coupling was improved with the doping of Zn in CuO_2 planes [12]. We had doped Zn in $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-\nu}Zn_{\nu}O_{12-\delta}$ (y=0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5) superconductors and achieved enhanced superconductivity with increased Zn doping [13]. These studies had shown that even if the anti-ferromagnetic lattice is replaced by spin-free 3d¹⁰ state of Zn, the superconductivity is enhanced, which is most likely brought about by decreased population of spin scattering of Cu atoms.

In the present study we have doped $4d^{10}$ Cd metal at the Cu site. The main objective of this substitution is to observe if there is any role of electron–phonon interactions in the mechanism of superconductivity. The electronic interactions of $4d^{10}$ Cd atoms with the free carriers would be identical to that of $3d^{10}$ Zn, but the atomic mass of Cd atoms is almost as double as that of the Cu and Zn atoms.

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Fig. 1. X-ray diffraction scans of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Cd_yO_{12-\delta}$ (y=0, 0.25, 0.5) superconductor.

The heavier atoms of Cd would most likely enhance an-harmonic oscillations in the CuO₂/CdO₂ planes and in turn decrease the population of desired number of phonons required for electron–phonon interactions. The un-availability of required density of phonons would suppress the critical temperature of the final compound. These an-harmonic processes would most likely decrease the Fermi velocity [$V_F = \pi \xi_c \Delta/\hbar$] of the carriers which in turn result into decreased coherence length [$\xi_c = \hbar^2 K_F/2m\Delta$] of the carriers and suppress the critical temperature of the final compound.

2. Experimental

The Cu_{0.5}Tl_{0.5}Ba₂Ca₃Cu_{4-y}Cd_yO_{12-δ} (y=0, 0.25, 0.5, 0.75, 1.0) superconductor samples were synthesized by solid-state reaction method, which was accomplished in two stages. At the first stage we have prepared Cu_{0.5}Ba₂Ca₃Cu_{4-y}Od_yO_{12-δ} (y=0, 0.25, 0.5, 0.75, 1.0) precursor material, by thoroughly mixing the Cd(NO₃)₂, Ba(NO₃)₂, Ca(NO₃)₂ and Cu(CN) compounds in appropriate ratios and grinding in a quartz mortar and pestle for an hour. The mixed material was fired twice; it was kept in quartz boat and loaded into a pre-heated furnace at 880 °C for 24 h followed by furnace cooling to room temperature and intermediate grinding. At the second stage, the fired precursor material was mixed with Tl₂O₃ and ground for about an hour to give Cu_{0.5}Tl_{0.5}Ba₂Ca₃Cu_{4-y}Cd_yO_{12-δ} (y=0, 0.25, 0.5, 0.75, 1.0) as final reactants composition. Thallium mixed material was pelletized under 3.8 tons/cm² pressure and the pellets were wrapped by a thin gold foil. These samples were heat treated for 10 min in a pre-heated furnace at 880 °C for 10 min the method.

The samples were characterized by resistivity measurements using four-probe method and ac-susceptibility measurements using mutual induction method. The structure of the material was determined by XRD using a Cu K α source of wavelength 1.54056 Å and the cell parameters were determined by a cell refinement computer



Fig. 2. (a) Resistivity measurements versus temperature of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3-Cu_{4-y}Cd_yO_{12-\delta}$ (y = 0, 0.25, 0.5) superconductors as prepared. (b) Resistivity measurements versus temperature of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Cd_yO_{12-\delta}$ (y = 0, 0.25, 0.5) superconductors after post-annealing in oxygen.

program. The FTIR absorption measurements were carried out using NICOLET spectrometer. The FTIR spectroscopy was carried out using KBr as a background material with 200 scans. In order to reduce the signal to noise ratio we have taken 500 scans in the sample spectrum. The post-annealing in flowing oxygen atmospheres was carried out in a tubular furnace at 500 °C for 5 h.

3. Results and discussion

The X-ray diffraction scans of Cu_{0.5}Tl_{0.5}Ba₂Ca₃Cu_{4-y}Cd_yO_{12- δ} (*y* = 0, 0.25, 0.5) superconductor samples are shown in Fig. 1. These samples have shown tetragonal structure and the diffraction lines are fitted following P4/mmm space group. The diffraction lines fitted to the computer program have shown *a*-axes length 4.146, 4.146 and 4.147 Å and *c*-axes length 17.86, 17.83 and 17.8 Å for *y* = 0, 0.25 and 0.5, respectively.

The resistivity measurements of these samples for (y = 0, 0.25, 0.5) are shown in Fig. 2a. All these (y = 0, 0.25, 0.5) samples have shown metallic variations of resistivity from room temperature down to onset of superconductivity [$T_c(onset)$] with onset of superconductivity at 125, 116 and 110 K and $T_c(R=0)$ at 109, 107.5 and 102 K, respectively. The resistivity measurements of these samples post-annealed in oxygen atmosphere are shown in Fig. 2b. Both the $T_c(onset)$ and $T_c(R=0)$ are shifted to higher temperature values. These samples have shown $T_c(onset)$ around 131, 124 and 120 K and $T_c(R=0)$ at 120, 114 and 115 K for y = 0, 0.25 and 0.5, respectively.

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