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Reduced anti-ferromagnetism promoted by Zn $3d^{10}$ substitution at CuO_2 planar sites of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ superconductors

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The role of charge carriers in ZnO_2/CuO_2 planes of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ material in bringing about superconductivity has been explained. Due to suppression of anti-ferromagnetic order with Zn $3d^{10}$ ($S=0$) substitution at Cu $3d^9$ ($S=\frac{1}{2}$) sites in the inner CuO_2 planes of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ superconductor, the distribution of charge carriers becomes homogeneous and optimum, which is evident from the enhanced superconductivity parameters. The decreased *c*-axis length with the increase of Zn doping improves interlayer coupling and hence the three dimensional (3D) conductivity in the unit cell is enhanced. Also the softening of phonon modes with the increased Zn doping indicates that the electron–phonon interaction has an essential role in the mechanism of high-T_c superconductivity in these compounds.

1. Introduction

Since the discovery of high temperature superconductivity in oxides, its mysterious mechanism could not be completely explained. Among the unresolved issues, the most important concerning to the cuprate superconductors is whether the distribution of carriers in CuO_2 planes is uniform or inhomogeneous. The first goal in the study of layered cuprate superconductors is always to find the optimum structure and content to reach the maximum possible critical temperature (T_c). The dependence of superconducting transition temperature (T_c) on the number of CuO_2 planes in multilayered cuprates is an interesting problem that can bring important information to understand the mechanism of high T_c superconductivity [1,2]. Up to now, there is a clear consensus, based on the structural studies and their correlation with superconducting properties, that the highest T_c's can be reached if there exist three CuO_2 planes and a small Cu–O in plane distance in the unit cell [3].

It has been suggested that in higher ordered layered cuprates, the existence of anti-ferromagnetic spins order of Cu atoms in the inner CuO_2 planes (IP) suppresses the superconductivity due to inhomogeneous charge carriers distribution in the planes [4–13]. The existence of anti-ferromagnetically aligned spins reduces the mobile carriers density and promotes the inhomogeneous carriers doping in the inner and outer planes of the cuprates. The results from nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements have shown a suppression of anti-ferromagnetic spin correlation with the Zn substitution in various high T_c superconductors [14–17]. Therefore, it is also expected to be true in $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ superconductor that Zn substitution would suppress the anti-ferromagnetism in the inner conducting planes. In the unit cell of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ superconductor, the two outer-pyramidal CuO_2 planes (OP) have five fold oxygen coordination and the inner-square CuO_2 planes (IP) have four fold oxygen coordination. It has been observed that OP are over-doped and the IP are under doped with carriers [11,18,19]. The OP have higher carriers density because of their presence in the vicinity of the $Cu_{0.5}Tl_{0.5}Ba_2O_{2n+4-\delta}$ charge reservoir layer. The IP are suggested to attain the anti-ferromagnetic state due to the deficiency of carriers [18,19]. NMR studies had shown that OP have higher, whereas IP have lower values of critical temperature (T_c) [10–13].

The main motivation behind this present research work is to reduce the anti-ferromagnetic order in the inner CuO_2 planes and

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to homogenize the charge carriers distribution by the substitution of $3d^{10}$ Zn atoms at $3d^9$ Cu atoms in CuO_2 planes of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ high T_c superconductor. In this manuscript, we have presented a summary of systematic studies of structural and superconducting properties of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ ($y = 0$, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5) material and tried to investigate any possible role of anti-ferromagnetism and homogeneous charge distribution in the mechanism of high-T_c superconductivity.

2. Experimental

The $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ ($y = 0$, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5) samples are prepared by solid-state reaction method accomplished in two stages. At the first stage $Cu_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ precursor material is synthesized by using $Ba(NO_3)_2$ (99%, Merck), $Ca(NO_3)_2$ (99%, Merck), MgO (99%, BDH Chemical Ltd., Poole England), $Cu_2(CN)_2$ (99%, BDH Chemical Ltd., Poole England) and ZnO (99.7%, BDH Chemical Ltd., Poole England) as starting compounds. These compounds are mixed in appropriate ratios and grinded in a quartz mortar and pestle for about an hour. After grinding, the material is loaded in a quartz boat for firing in a furnace at 880 °C. The material is fired twice following one hour intermediate grinding. The precursor material is then mixed with Tl_2O_3 (99%, Merck) to give $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ as final reactant composition. Thallium oxide mixed precursor material is pelletized under 3.8 t/cm^2 pressure. The pellets are wrapped in a thin gold foil and sintered at respective temperatures for 10 min, followed by quenching to room temperature. The rectangular bar shaped samples of dimensions 2 mm × 2.5 mm × 10 mm are used for dc-resistivity and ac-susceptibility measurements. The structure of the material is determined by using X-ray diffraction scan (D/Max IIIC Rigaku with a CuK$_\alpha$ source of wavelength 1.54056 Å) and cell parameters by using a computer program. The phonon modes related to the vibrations of various oxygen atoms in $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ unit cell were observed by Nicolet 5700 Fourier transform infrared (FTIR) spectrometer in the 400–650 cm^{-1} wavenumber range. The dc-resistivity and IV characteristics of the samples are measured by four-probe technique. The ac-susceptibility measurements are carried out by mutual inductance method using SR530 Lock-in Amplifier at a frequency of 270 Hz with $H_{AC} = 0.7$ Oe of primary coil. The oxygen content of the samples were determined by standard iodometric titration method [20–22].

3. Results and discussion

The X-ray diffraction patterns of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ ($y = 0$, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5) samples have shown single phase tetragonal structure with good quality in all Zn doping level. The variation of c-axis lengths with Zn doping (at%) is shown in Fig. 1. The substational decrease in the c-axis length with the increase of Zn concentration reflects the improvements of interlayer coupling due to which carriers density in the planes becomes homogeneous and optimum. Also the decreased c-axis length increases the coherence length along c-axis resulting into a decrease in the anisotropy [23–26], which increases the mean free path of carriers and improve their three dimensional (3D) conductivity. The decrease in the c-axis length may be due to the Jhan–Teller effect [27,28]. The Cu^{+2} ions exhibit a strong Jahn–Teller effect; the octahedron around Cu^{+2} is elongated along c-axis [29]. However, the octahedron around Zn^{+2} is not distorted, since Zn^{+2} is in the d^{10} state. Therefore, doping of Zn at Cu sites

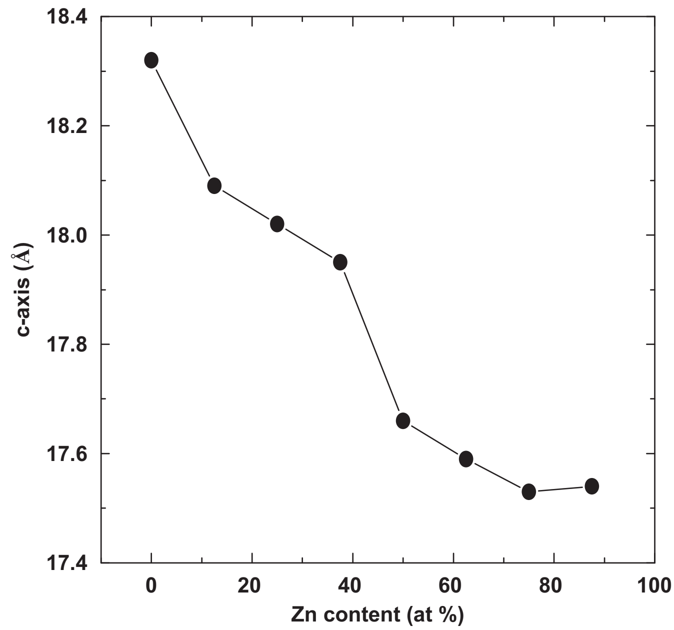

Fig. 1. Variation of c-axis lengths versus Zn content (at%) in $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_{4-y}Zn_yO_{12-\delta}$ superconductors.

will reduce the local Jahn–Teller distortion, and hence reduces the c-axis length. The substantial decrease in c-axes length with Zn substitution suppresses the volume of the unit cell and hence increases the Fermi wavevector [$K_F = (3\pi^2(N/V))^{1/3}$]. The reduction of the volume of the unit cell due to the decrease in c-axes length is a clear evidence of enhanced interlayer coupling. Also due to an increase in the K_F, the coherence length along c-axis ($\xi_c = \hbar K_F/2m\Delta$) is increased, which in turn increases the Fermi velocity of the carriers ($v_F = \pi\xi_c\Delta/\hbar$); v_F is the Fermi velocity of the carriers and Δ is pairing potential. The increased Fermi velocity along c-axis possibly enhances the superconductivity parameters. Zinc substitution decreases the c-axis length due to which coherence length decreases and 3D conductivity in the unit cell is improved. It is, therefore, the reduction of c-axis length, which improves 3D conductivity and the homogeneous distribution of the carriers in the conducting CuO_2/ZnO_2 planes. Interestingly, the decrease in c-axis length seems to correlate with T_c because the variation of c-axis length is nearly on the same pattern as the increase in T_c with the increase of Zn doping in $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ superconductors. If this correlation is real, then the Jahn–Teller distortion may play an important role in the superconductivity mechanism.

The apical oxygen phonon modes of type Tl-O_A-M(2) and Cu(1)-O_A-M(2) {where M = Cu/Zn} are softened from 501 and 537 to 454 and 514 cm^{-1} respectively with increased Zn doping at Cu sites in CuO_2 planes of $Cu_{0.5}Tl_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ superconductor, Fig. 2(a). The planar oxygen phonon modes of type M(2)-O_P-M(2) are also softened from 575 to 564 cm^{-1} with the increase of Zn concentration in the unit cell, Fig. 2(b). If the softening of these oxygen modes is linked with the decreased c-axis length then it becomes evident that the bond lengths along c-axis are decreased between the planes because the net magnetic spin distortion is minimized with Zn $3d^{10}$ substitution. The softening of these modes is most probably linked with the increased mass of Zn (65.38 amu) as compared to that of Cu (63.54 amu) [30]. However, the apical oxygen bond length is suppressed with Zn doping due to the reduction of Jahn–Teller distortion but the effect of increased mass of Zn is more prominent in softening these modes. The Jahn–Teller distortion is interaction of spin lattice