

Homogeneous distribution of carriers in the conducting planes by Zn substitution at Cu sites in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductors

M. Mumtaz and Nawazish A. Khan

Materials Science Laboratory, Department of Physics, Quaid-i-Azam University, Islamabad 45320, Pakistan
E-mail: mmumtaz75@yahoo.com

Received May 15, 2009, revised July 21, 2009

The effect of suppression of antiferromagnetic order and charge stripes formation mechanism, by $\text{Zn}3d^{10}$ ($S = 0$) substitution at $\text{Cu}3d^9$ ($S = 1/2$) sites in CuO_2 planes of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$, on superconductivity parameters is demonstrated. If antiferromagnetism and charge stripes have some role in bringing about superconductivity at a particular temperature, the doping of nonmagnetic Zn impurity would destroy it and hence the superconductivity. However we have observed enhanced superconducting properties with the increase of Zn doping in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor. The decreased c -axis length with the increase of Zn doping improves interlayer coupling and hence the three-dimensional conductivity in the unit cell. The role of charge carriers in CuO_2 planes of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ in bringing about superconductivity has also been explained.

PACS: **74.70.-b** Superconducting materials other than cuprates;
74.62.Bf Effects of material synthesis, crystal structure, and chemical composition;
74.25.Uv Vortex phases (includes vortex lattices, vortex liquids, and vortex glasses).

Keywords: $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ superconductors, antiferromagnetism, charge stripes, charge carriers.

1. Introduction

After the discovery of high temperature superconductivity in oxides (i.e La-based) by Bednorz and Muller in 1986, different theories, models, suggestions, and opinions came from the different corners of the scientific community, but unfortunately up till now none of them can 100% explain the mysterious mechanism of high temperature superconductivity. Among the unresolved issues in high T_c cuprates, the most important are:

- (1) Antiferromagnetic order in CuO_2 planes of layered cuprates.
- (2) Non-homogeneous carrier distribution in CuO_2 planes.
- (3) Charge stripes.

It has been suggested that in layered cuprates, the presence of antiferromagnetic order in CuO_2 planes suppresses the superconductivity and this effect becomes more prominent when the number of CuO_2 planes increases beyond three [1–7]. The results from nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements show the suppression of antiferromagnetic spin correlation by Zn substitution in various high T_c superconductors [8–11]. Therefore, it is expected to be true in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor that Zn substitu-

tion suppresses the antiferromagnetic order in conducting planes. In the unit cell of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$, 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. NMR experiments have shown that OP are over-doped and the IP are underdoped with carriers [5,12,13]. It has also been found by NMR studies that OP have higher, whereas IP have lower values of critical temperature T_c [4–7]. The OP have higher carriers density because of their presence in the vicinity of the $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{O}_{2n+4-\delta}$ charge reservoir layer. The IP are suggested to attain the antiferromagnetic state due to the deficiency of carriers [12,13].

In second opinion, the movement of charge stripes formed due to the magnetic interaction of the $3d^9$ electrons of Cu atoms in CuO_2 planes promotes the superconductivity [14,15]. Stripes are microscopic rivers of charges that flow in superconductors. A stripe order is the state, where spins and charges become ordered simultaneously. In the stripe phase, there is periodic arrangement of charge stripe and spin stripes [14]. The basic physics of stripe formation is the expulsion of holes from the regions of well-formed local moments [16]. In one scenario the holes would like to separate themselves completely from the spins [17,18].

However, the long range Coulomb repulsion frustrates this tendency, and stripes appear as a compromise. In another view [19,20], short-range interaction can lead to stripe formation. Beyond stripology, the key question is the role of stripes in superconductivity. There is an evidence of presence of static stripes, or some form of local magnetic order in superconducting samples [22–25]. However, it generally appears that the static stripes are antipathetic to superconductivity and dynamical stripes promote superconductivity [15].

The motivation of present work is to reduce the antiferromagnetic order in CuO_2 planes and also to observe what will happen with the superconductivity when charge stripe formation mechanism is quenched by the substitution of $3d^{10}$ Zn atoms having zero remnant spins at $3d^9$ Cu atoms in CuO_2 planes of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ high T_c superconductors. Also we would like to observe the role of carriers in bringing about the superconductivity in Zn substituted $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor. For these purposes Zn is doped at Cu sites in CuO_2 planes of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor and the systematic increase in almost all the superconducting properties is observed [26–35]. In this article, we have presented a gist of the results of systematic study of structure and superconducting properties of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ ($y = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5$) material and tried to investigate the role of antiferromagnetism and charge stripes in high T_c superconductivity by quenching these mechanisms with Zn substitution at Cu sites in CuO_2 planes of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor.

2. Experimental

The $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ ($y = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5$) samples were prepared by solid-state reaction method accomplished in two stages. At the first stage $\text{Cu}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ precursor material is synthesized by using $\text{Ba}(\text{NO}_3)_2$ (99%, Merck), $\text{Ca}(\text{NO}_3)_2$ (99%, Merck), MgO (99%, BDH Chemical Ltd. Poole England), $\text{Cu}_2(\text{CN})_2$ (99%, BDH Chemical Ltd. Poole England) and ZnO (99.7%, BDH Chemical Ltd. Poole England) as starting compounds. These compounds were mixed in appropriate ratios and grinded in a quartz mortar and pestle for about an hour. After grinding, the material was loaded in a quartz boat for firing in a furnace at 880°C . The material was fired twice following one hour intermediate grinding. The precursor material was then mixed with Tl_2O_3 (99%, Merck) to give $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ as final reactant composition. Thallium oxide mixed precursor material was pelletized under 3.8 tons/cm^2 pressure. The pellets were wrapped in a thin gold foil and sintered at respective temperatures for 10 minutes, followed by quenching to room temperature. The rectangular bar shaped samples of dimensions $2 \times 2.5 \times 10\text{ mm}$ were used for dc-resistivity and ac-susceptibility measurements. The structure of material were determined by using x-ray diffraction scan (D/Max

III C Rigaku with a CuK_α source of wavelength 1.54056 \AA) and cell parameters by using a computer program. The phonon modes related to the vibrations of various oxygen atoms in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ unit cell were observed by Nicolet 5700 Fourier transform infrared (FTIR) spectrometer in the $400\text{--}650\text{ cm}^{-1}$ wave number range. The dc-resistivity and IV characteristics of the samples are measured by four-probe technique. The ac-susceptibility measurements were carried out by mutual inductance method using S.R.530 Lock-in Amplifier at a frequency of 270 Hz with $H_{AC} = 0.7\text{ Oe}$ of primary coil.

3. Results and discussion

The x-ray diffraction patterns of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ ($y = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5$) samples indicate that all the samples are almost single phase with good quality in all Zn doping level having the tetragonal structure. The variation of c -axis lengths with Zn content (at.%) is shown in Fig. 1. The substantial 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 decreased c -axis length reduces the anisotropy and increases the coherence length along c -axis [36–39] due to which carriers mean free path decreases and three dimensional (3D) conductivity is improved. Further interplane coupling is improved by Mg substitution at Ca sites in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_2\text{Cu}_{3-y}\text{Zn}_y\text{O}_{10-\delta}$ superconductors [28,29]. The decrease in the c -axis length may be due to the Jahn-Teller effect [40,41]. The Cu^{+2} ions exhibit a strong Jahn-Teller effect; the octahedron around Cu^{+2} is elongated along c -axis [42]. However, the octahedron around Zn^{+2} is not distorted since Zn^{+2} is in d^{10} state. Therefore, doping the Cu sites with Zn will reduce the local Jahn-Teller distortion, and hence reduces the c -axis length. 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

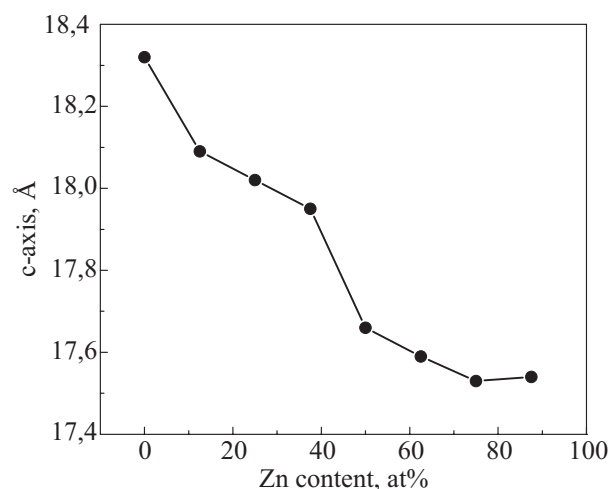


Fig. 1. Variation of c -axis lengths versus Zn content (at.%) in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ superconductors.

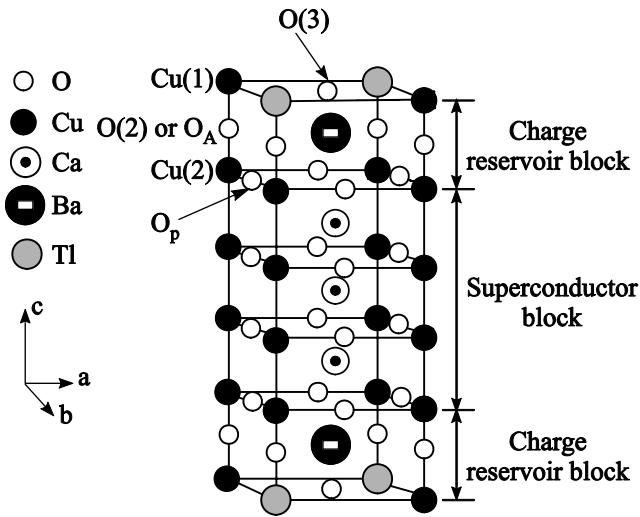


Fig. 2. Unit cell of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor.

pattern as the increase in T_c with the increase of Zn doping in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ system. If this correlation is real, then the Jhan-Teller distortion may play an important role in the superconductivity mechanism.

The unit cell of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor is shown in Fig. 2. The apical oxygen phonon modes of type $\text{Tl-O}_A\text{-M}(2)$ and $\text{Cu}(1)\text{-O}_A\text{-M}(2)$ (where $M = \text{Cu}/\text{Zn}$) are seemed to be softened from 501 and 537 cm^{-1} to 454 and 514 cm^{-1} , respectively with Zn doping at Cu sites in CuO_2 planes of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-\delta}$ superconductor, Fig. 3,a. The planar oxygen phonon modes of type $\text{M}(2)\text{-O}_p\text{-M}(2)$ are also softened from 575 cm^{-1} to 564 cm^{-1} with the increase of Zn concentration in the unit cell, Fig. 3,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 $\text{Zn}3d^{10}$ substitution in the planes. The softening of these modes is most probably due to increased mass of Zn (65.38 amu) as compared to that of Cu (63.54 amu) [34]. However, the apical oxygen bond length is suppressed with Zn doping due to the reduction of Jhan-Teller distortion but the effect of increased mass of Zn is more prominent in softening these modes. The variation of these modes of oxygen reflects the new interaction of oxygen with its environments in the unit cell of this new material.

The variation of zero resistivity critical temperature T_c and normal state resistivity at room temperature ($\rho_{290\text{K}}(\Omega\cdot\text{cm})$) with the Zn content (at.%) in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ superconductors is shown in Fig. 4,a. The variation of the resistivity with temperature is metallic from room temperature down to onset of superconductivity for all the samples [26–35]. In Zn free sample the zero resistivity critical temperature $T_c(R = 0)$ is observed around 108 K, which is increased to 110, 112, 113, 117, 120, 122, and 124 K for the samples with Zn doping concentrations of $y = 0, 0.5, 1.0,$

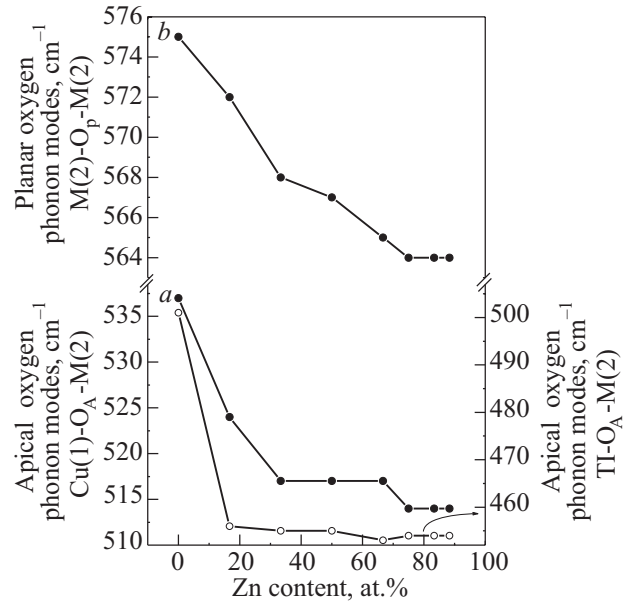


Fig. 3. Variation of apical oxygen phonon modes versus Zn content (at.%) in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ superconductors (a). Variation of planar oxygen phonon modes versus Zn content (at.%) in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ superconductors (b).

1.5, 2.0, 2.5, 3.0, and 3.5, respectively. Also the normal state resistivity at room temperature decreases from 0.14 to $0.04\ \Omega\cdot\text{cm}$ with the increase of Zn doping concentration from $y = 0$ to $y = 3.5$. These are the intrinsic properties of

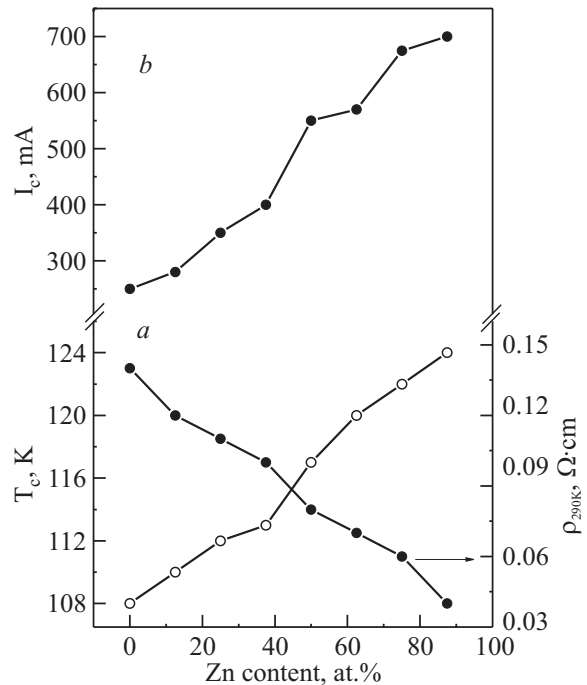


Fig. 4. Variation of zero resistivity critical temperature T_c and normal state resistivity at room temperature ($\rho_{290\text{K}}(\Omega\cdot\text{cm})$) versus Zn content (at.%) in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ superconductors (a). Variation of critical current (I_c) observed from IV characteristics of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-\delta}$ superconductors versus Zn content (at.%) (b).

this new material, which are repeatedly confirmed and most probably due to optimization and homogeneous distribution of carriers in the conducting planes. There are many factors affecting the normal state resistivity ($\rho_{290\text{K}}$ ($\Omega\cdot\text{cm}$)) of the superconducting materials. One of them is the reduction of defects in the crystal structure due to Zn doping as evident from XRD pattern [32,34]. It may be quite possible that the major contribution to the reduction of $\rho_{290\text{K}}$ ($\Omega\cdot\text{cm}$) is due to less scattering of carriers by the phonons due to Zn doping at room temperature. Due to the zero remnant magnetic spin of Zn $3d^{10}$, no carriers scattering takes place and carrier density goes to the optimum level in the conducting planes and hence T_c of the material is increased.

Also the IV-characteristics of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-8}$ samples represent the systematic increase in transport critical current (I_c) with the increase of Zn doping as shown in Fig. 4,b. These measurements show the improvement of grain connectivity and we can say that grain boundaries become more conductive with Zn doping. The weak connectivity of grains can reduce the overlap of the wavefunctions of the carriers in the adjacent grains bringing about superconductivity and can suppress the order parameter [43]. In polycrystalline materials, the most probable sources of weak links through grain boundaries are oxygen deficiency, vacancies, secondary phases, impurity phases composition variation, disorientation of grain boundaries etc [44–48]. The elimination of these sources would increase the coupling between the grains and hence the transport properties of oxide superconductors. The weak links promote inferior transport properties in the compound [49–51]. The maximum transport current (in zero/non-zero external magnetic field) is an important parameter, which sets a criterion for the superconductor to be used for applications. As in our samples the impurity phases are nominal and other sources may be decreased with Zn substitution, so transport properties are increased.

The ac-susceptibility measurements of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-8}$ samples complement the resistivity measurements that T_c onset and peak temperature T_p observed in out of phase component are seemed to be increased with the increase of Zn doping level as shown in Fig. 5,a. The relative increase in the diamagnetic signal normalized with the masses of the samples versus Zn content (at.%) is shown in Fig. 5,b. It is also observed that diamagnetic transition becomes sharp with the increase of Zn concentration, which is the finger print of improvement of the single phase stability with Zn substitution [26–35]. The ac-susceptibility measurements provide the information about the volume superconductivity by the diamagnetic behaviour of the material. So the volume superconductivity is improved with Zn substitution, which may be due to increase in coherence length along c -axis and homogeneous distribution of carriers with less perturbation in the planes. The in-phase component of magnetic ac-susceptibility χ' is related to Meissner volume of the diamagnetism within the grains [43,44,52]. The suppression of superconductivity within the grains decreases the mag-

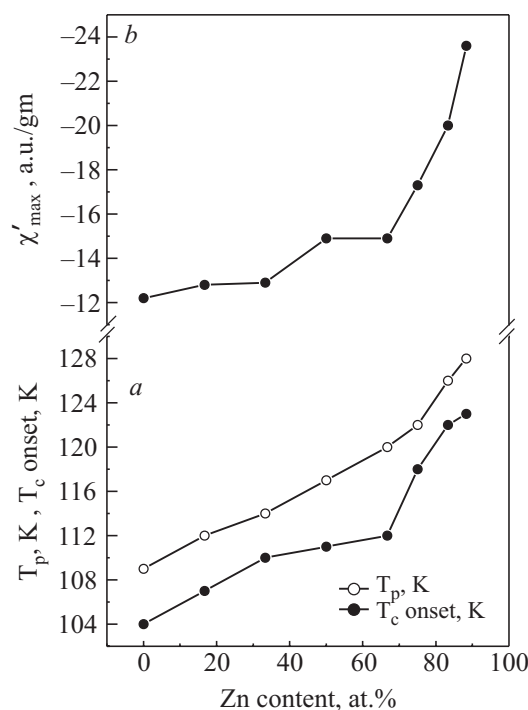


Fig. 5. Variation of T_c onset and peak temperature (T_p) observed in out-of-phase component of ac-susceptibility versus Zn content (at.%) in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-8}$ superconductors (a). Variation of maximum diamagnetic signal observed in in-phase component of ac-susceptibility versus Zn content (at.%) in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-8}$ superconductors (b).

nitude of χ' . The χ' originates from the superconducting shielding currents, which flow over the surface of the sample. The imaginary part of magnetic ac-susceptibility χ'' measures the hysteresis losses due to eddy currents through the inter-grain weak links. The peak of χ'' in a superconductor with weakly connected grains appeared at lower temperatures as compared to the sample with strongly coupled grains [53]. The sharpness of the peak in χ'' reflects the strong intergrain coupling, flux pinning and higher J_c in the samples [54,55].

The carriers, in case of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-8}$ superconductors, are most likely supplied by the ratio of $\text{Cu}^{+2}/\text{Tl}^{+3}$ and oxygen content in the $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{O}_{4-8}$ charge reservoir layers [32,34]. Oxygen content, determined by standard iodometric titration [56,57], are increased with the Zn doping in the unit cell. The presence of Cu^{+2} in the $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{O}_{4-8}$ charge reservoir layers of $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_3\text{Cu}_{4-y}\text{Zn}_y\text{O}_{12-8}$ efficiently dopes the $\text{ZnO}_2/\text{CuO}_2$ planes with carriers and we get enhanced superconductivity. The most possible reason for the enhanced superconducting properties is the reduction of the anisotropy due to decreased c -axis length of the material with Zn doping, which decreases the carriers mean free path and carriers density becomes homogeneous and optimum in the conducting planes.

4. Conclusion

The doping of Zn $3d^{10}$ at Cu $3d^9$ sites in CuO₂ planes of Cu_{0.5}Tl_{0.5}Ba₂Ca₃Cu₄O₁₂₋₈ superconductor enhances the superconductivity parameters, which is most probably due to homogeneous distribution of carriers in the conducting planes by the suppression of antiferromagnetic order and charge stripes mechanism. The Zn substitution decreases the *c*-axis length due to which coherence length decreases, carrier distribution in the planes becomes homogeneous and optimum, and 3D conductivity in the unit cell is improved. So the role of charge carriers in high *T_c* superconductivity is primary. Also the grain connectivity becomes better and single phase stability is improved with Zn substitution in the material.

1. H. Kotegawa, Y. Tokunaga, K. Ishida, G.-Q. Zheng, Y. Kitaoka, H. Kito, A. Iyo, K. Tokiwa, T. Watanabe, and H. Ihara, *Phys. Rev.* **B64**, 064515 (2001).
2. H. Kotegawa, Y. Kitaoka, Y. Araki, Y. Tokunaga, G.-Q. Zheng, K. Tokiwa, T. Watanabe, A. Iyo, H. Kito, Y. Tanaka, and H. Ihara, *Physica* **C408**, 761 (2004).
3. A. Trokiner, L. Le. Noc, J. Schneck, A.M. Pougnet, R. Mellet, J. Primot, H. Savary, Y.M. Gao, and S. Aubry, *Phys. Rev.* **B44**, 2426 (1991).
4. Y. Tokunaga, H. Kotegawa, K. Ishida, G.-Q. Zheng, Y. Kitaoka, K. Tokiwa, A. Iyo, and H. Ihara, *J. Low Temp. Phys.* **117**, 473 (1999).
5. Y. Tokunaga, K. Ishida, Y. Kitaoka, K. Asayama, K. Tokiwa, A. Iyo, and H. Ihara, *Phys. Rev.* **B61**, 9707 (2000).
6. H. Kotegawa, Y. Tokunaga, K. Ishida, G.-Q. Zheng, Y. Kitaoka, K. Asayama, H. Kito, A. Iyo, H. Ihara, K. Tanaka, K. Tokiwa, and T. Watanabe, *J. Phys. Chem. Solids* **62**, 171 (2001).
7. N. Hamada and H. Ihara, *Physica* **C357**, 108 (2001).
8. K. Ishida, Y. Kitaoka, N.O. Gata, T. Kaminto, K. Asayama, J.R. Cooper, and N. Athanassopoulou, *J. Phys. Soc. Jpn.* **62**, 2803 (1993).
9. T.K. Park, B.J. Mean, K.H. Lee, G.S. Go, S.W. Seo, K.S. Han, M. Lee, H.S. Lee, H.B. Kim, and W.C. Lee, *Phys. Rev.* **B59**, 11217 (1999).
10. G. Zheng, T. Odaguchi, T. Mito, Y. Kitaoka, K. Asayama, and Y. Kodama, *J. Phys. Soc. Jpn.* **62**, 2591 (1993).
11. G.V.M. Williams, and S. Krämer, *Phys. Rev.* **B64**, 104506 (2001).
12. H. Adrian and S. Nidsen, *Eur. Phys. Lett.* **5**, 265 (1988).
13. K. Tokiwa, S. Ito, H. Okumoto, S. Mikusu, A. Iyo, Y. Tanaka, and T. Watanabe, *J. Low Temp. Phys.* **131**, 637 (2003).
14. O. Anegawa, Y. Okajima, S. Tanda, and K. Yamaya, *Phys. Rev.* **B63**, 140506 (2001).
15. V.J. Emery, S.A. Kivelson, and O. Zachar, *Phys. Rev.* **B56**, 6120 (1997).
16. J. Orenstein and A.J. Millis, *Science* **288**, 468 (2000).
17. V.J. Emery, S.A. Kivelson, and H.-Q. Lin, *Physica B* **163**, 306 (1990); *Phys. Rev. Lett.* **64**, 475 (1990).
18. U. Low, V.J. Emery, K. Fabricius, and S.A. Kivelson, *Phys. Rev. Lett.* **72**, 1918 (1990).
19. J. Zaanen, *J. Phys. Chem. Solids* **59**, 1769 (1998).
20. S.R. White, and D.J. Scalapino, *Phys. Rev.* **B61**, 6320 (2000).
21. G. Siebold, C. Castellani, D. DiCastro, and M. Grilli, *Phys. Rev.* **B58**, 13506 (1998).
22. J. Tranquada, B.J. Sternlieb, J.D. Axe, Y. Nakamura, and S. Uchida, *Nature* **375**, 561 (1995).
23. J. Tranquada *et al.*, *Phys. Rev. Lett.* **78**, 338 (1997); J. Tranquada *et al.*, *Physica B* **241–243**, 475 (1997).
24. T. Suzuki, T. Goto, K. Chiba, T. Shinoda, T. Fukase, H. Kimura, K. Yamada, M. Ohashi and Y. Yamaguchi, *Phys. Rev.* **B57**, 3229 (1997); H. Kimura, K. Hirota, H. Matsushita, K. Yamada, Sung-Hun Lee, Ch.F. Majkrzak, R. Erwin, G. Shirane, M. Greven, Young S. Lee, M.A. Kastner, and R.J. Birgeneau, *Phys. Rev.* **B59**, 6517 (1999).
25. Ch. Niedermayer, C. Bernhard, T. Blasius, A. Golnik, A. Moodenbaugh, and J.I. Budnick, *Phys. Rev. Lett.* **80**, 3843 (1998).
26. Nawazish A. Khan, and M. Mumtaz, *Supercond. Sci. Technol.* **19**, 762 (2006).
27. Nawazish A. Khan and M. Mumtaz, *Eur. Phys. J. Appl. Phys.* **38**, 47 (2007).
28. Nawazish A. Khan and M. Mumtaz, *Mater. Lett.* **62**, 659 (2008).
29. M. Mumtaz and Nawazish A. Khan, *J. Appl. Phys.* **103**, 083913 (2008).
30. Nawazish A. Khan, M. Mumtaz, M.M. Ahadian, and Azam Irajizad, *Physica C* **453**, 46 (2007).
31. M. Mumtaz and Nawazish A. Khan, *Supercond. Sci. Technol.* **20**, 1228 (2007).
32. Nawazish A. Khan and M. Mumtaz, *J. Low Temp. Phys.* **149**, 97 (2007).
33. M. Mumtaz, and Nawazish A. Khan, *Supercond. Sci. Technol.* **21**, 065015 (2008).
34. Nawazish A. Khan and M. Mumtaz, *Phys. Rev.* **B77**, 054507 (2008).
35. Nawazish A. Khan, M. Mumtaz, and A.A. Khurram, *J. Appl. Phys.* **104**, 033916 (2008).
36. H. Ihara, *Physica C* **364–365**, 289 (2001).
37. H. Ihara, A. Iyo, K. Tanaka, K. Tokiwa, N. Terada, M. Tokumoto, K. Ishida, and M. Umeda, *Adv. Supercond.* **I.X**, 277 (1996).
38. H. Ihara, A. Iyo, K. Tanaka, K. Tokiwa, K. Ishida, N. Terada, M. Tokumoto, Y. Sekita, T. Tsukamoto, T. Watanabe, and M. Umeda, *Physica C* **282–287**, 1973 (1997).
39. M. Tinkham, *Introduction to Superconductivity*, McGraw-Hill, Inc., New York (1996).
40. T.M. Tarascon, L.H. Greene, P. barboux, W.R. McKinnon, G.W. Hull, T.P. Orlando, K.A. Delin, S. Foner, and E.J. McNiff, Jr., *Phys. Rev.* **B36**, 8393 (1987).
41. L.E. Orgel, *An Introduction to Transition-Metal Chemistry: Ligand-Field Theory*, Methuen, London (1960).
42. G. Xiao, A. Bakhshai, Marta Z. Cieplak, Z. Tesanovic, and C.L. Chien, *Phys. Rev.* **B39**, 315 (1989).
43. S.K. Agarwal and B.V. Kumaraswamy, *J. Phys. Chem. Solids* **66**, 729 (2005).
44. H. Salamati and P. Kameli, *Solid State Commun.* **125**, 407 (2003).
45. H. Salamati, A.A. Babaei-Brojeny, and M. Safa, *Supercond. Sci. Technol.* **14**, 816 (2001).

46. C.A.C. Passos, M.T.D. Orlando, A.A.R. Fernandes, F.D.C. Oliveira, D.S.L. Simonetti, J.F. Fardin, H. Belich Jr., and M.M. Ferreira Jr., *Physica C* **419**, 25 (2005).
47. M.A. Schofield, M. Beleggia, Y. Zhu, K. Guth, and C. Jooss, *Phys. Rev. Lett.* **92**, 195502 (2004).
48. M. Tepe, I. Avci, H. Kocoglu, and D. Abukay, *Solid State Commun.* **131**, 319 (2004).
49. A. Kunold, M. Hernandez, A. Myszkowski, J.L. Cardoso, and P. Pereyra, *Physica C* **370**, 63 (2002).
50. D. Shi, J.G. Chen, M. Xu, A.L. Cornelius, U. Balachandran, and K.C. Goretta, *Supercond. Sci. Technol.* **3**, 222 (1990).
51. M. Yang, Y.H. Kao, Y. Xin, and K.W. Wong, *Phys. Rev.* **B50**, 13653 (1994).
52. F. Gömöry, *Supercond. Sci. Technol.* **10**, 523 (1997).
53. A. Sedky, M.I. Youssif, S.M. Khalil, and A. Sawalha, *Solid State Commun.* **139**, 126 (2006).
54. R.V. Sarmago, K.L.C. Molina, and L.J.D. Guerra, *Physica C* **364**, 239 (2001).
55. Nawazish A. Khan, A.A. Khurram, and A. Maqsood, *Physica C* **398**, 114 (2003).
56. M. Karppinen, A. Fukuoka, L. Niinistö, and H. Yamauchi, *Supercond. Sci. Technol.* **9**, 121 (1996).
57. D.C. Harris, M.E. Hills, and T.A. Hewston, *J. Chem. Educ.* **64**, 847 (1987).