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Enhanced superconducting properties of Ti doped $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ samples

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Abstract

Ti-doped $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75, 1.0) superconductors have been synthesized by solid state reaction method. The prepared samples are characterized by XRD, electrical resistivity, AC susceptibility and FTIR techniques. XRD analysis showed that the lattice parameters are marginally altered but there is no substantial change with the doping of Ti. All the samples are found with orthorhombic crystal structure following PMMM space group. $T_c(R=0)$ is enhanced with the doping of Ti except for x = 1.0 sample. The magnitude of diamagnetism in the AC-susceptibility measurements is enhanced up to x = 0.5 and decreased beyond. The FTIR measurements show that the apical oxygen phonon modes are softened. The planar oxygen phonon modes are softened but their intensity is raised with the enhanced Ti contents. This softening of the planar oxygen phonon modes may be arising due to the heavier Ti ions (47.9 amu) at the lighter Ca (40.07 amu) sites. Variation in the lattice parameters in the XRD data and shifting of various oxygen phonon modes in the FTIR data show that Ti is incorporated at Ca sites in the unit cell. Increase in the superconducting properties up to certain doping level (x = 0.75) may be arising due to the improved interplane coupling caused by the smaller sized Ti at Ca sites. While the decrease in T_c and magnitude of diamagnetism beyond x = 0.75 and x = 0.5 respectively, is attributed to the suppressed density of a particular type of phonons required for optimum superconductivity. This suppression in the density of the desired phonons is brought about by the substitution of heavier Ti ions at the lighter Ca sites. This study signifies the role of electron–phonon interaction in mechanism of high T_c superconductivity.

1 Introduction

The major challenge in the cuprate high-temperature superconductors (HTSCS) is to understand the mechanism of superconductivity. Regarding this issue, the main focus of the researchers has been the unit cell of CuTl-1223 HTSCS [1–4]. The unit cell of (CuTl)-based HTSCS has two parts: (i) the semi-conducting charge reservoir layer $(Cu_{0.5}Tl_{0.5})Ba_2O_{4-\delta}$ and (ii) the superconducting CuO_2 planes. The Ba atoms separate the charge reservoir and superconducting planes, while Ca atoms separate the CuO_2 superconducting planes [5]. To supply the carriers, charge reservoir layers play a vital role, while CuO_2 planes are responsible for superconductivity [6].

Previously we have partially substituted Ca^{2+} ions by Mg^{2+} and Pr^{3+} ions in (Cu, Tl)-1223 samples. For Mg^{2+} suppressed *c*-axis length and softening in the apical oxygen phonon modes were observed. The inter-plane coupling, critical transition temperature $T_c(R=0)$ and critical current density J_c were enhanced for increasing Mg contents. On the other hand, an elongation in the crystal lattice parameter c, a weak coupling of the CuO_2-planes and decreased value of T_c were observed due to the Pr-substitution [7].

In the current work we substituted Ca by Ti at the interplane sites in the unit cell of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75, 1.0) samples. In the long coherence length and enhanced superconducting properties of Cu-Tl based high temperature superconductors the Fermi vector play a vital role, which itself depends on the density of cooper pairs and hence the phonons' population. In case

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of unavailability of essential phonons population the density of phonons is expected to be suppressed. This suppression in the phonon's density can lead to the suppressed Fermi vector and hence the coherence length. Ti has smaller ionic radii (0.9 Å) in comparison to Ca (0.99 Å) and higher electro negativity and hence may lead to strong interplane coupling [8]. On the other hand the atomic mass of Ti (47.9 amu) is greater than that of Ca (40.07 amu). Due the difference in masses of Ti and Ca it is expected that the Ti atoms being doped would produce anharmonic vibrations that would lead to the suppression of the desired phonon density and hence would help to understand the role of atomic mass (electron–phonon interaction) in the mechanism of superconductivity [9–15].

2 Experimental

We have used solid-state reaction method to synthesize Ti-doped $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75, 1.0) superconductors. This reaction comprises of two steps. The first step involves the preparation of precursor material by mixing and grinding $Ba(NO_3)_2$, $Ca(NO_3)_2$, TiO_2 and Cu(CN) for 1 h in a quartz mortar and pestle in appropriate ratios as a starting compound. The precursor material was then loaded into quartz boat, and fired twice in chamber furnace for 24 h at 860 °C involving intermediate grinding. In the second step Tl_2O_3 was mixed with the precursor material by grinding for about an hour in order to obtain final composition of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75, 1.0) superconductors. The powder was pressed into pellets at 5 tons/cm^2 pressure and were then enclosed in a gold capsule to reduce the loss of thallium and sintered for 10 min at 860 °C followed by quenching to room temperature.

For characterization of the samples, X-ray diffraction, four probe resistivity, AC-susceptibility and Fourier transform infrared spectroscopy (FTIR) techniques were used. The structural characterization was done by employing X-ray diffractometer (BRUKER D8 Focus) using Cu-Kα (λ = 1.5406 Å) radiation. Cell refinement computer program was used for the determination of crystal lattice constants. Temperature dependent dc-electrical resistivity measurement for all the prepared samples was carried out using the four-probe technique. To calculate the magnitude of diamagnetic susceptibility, AC-susceptibility technique at lock-in frequency of 270 Hz was used. The various oxygen phonon modes were investigated by using Nicolet 5700 FTIR spectrometer in the wave number range 400–620 cm^{-}.

3 Results and discussion

The X-ray diffraction patterns of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75, 1.0) samples are shown in Fig. 1. XRD scans reveal that most lines are indexed to

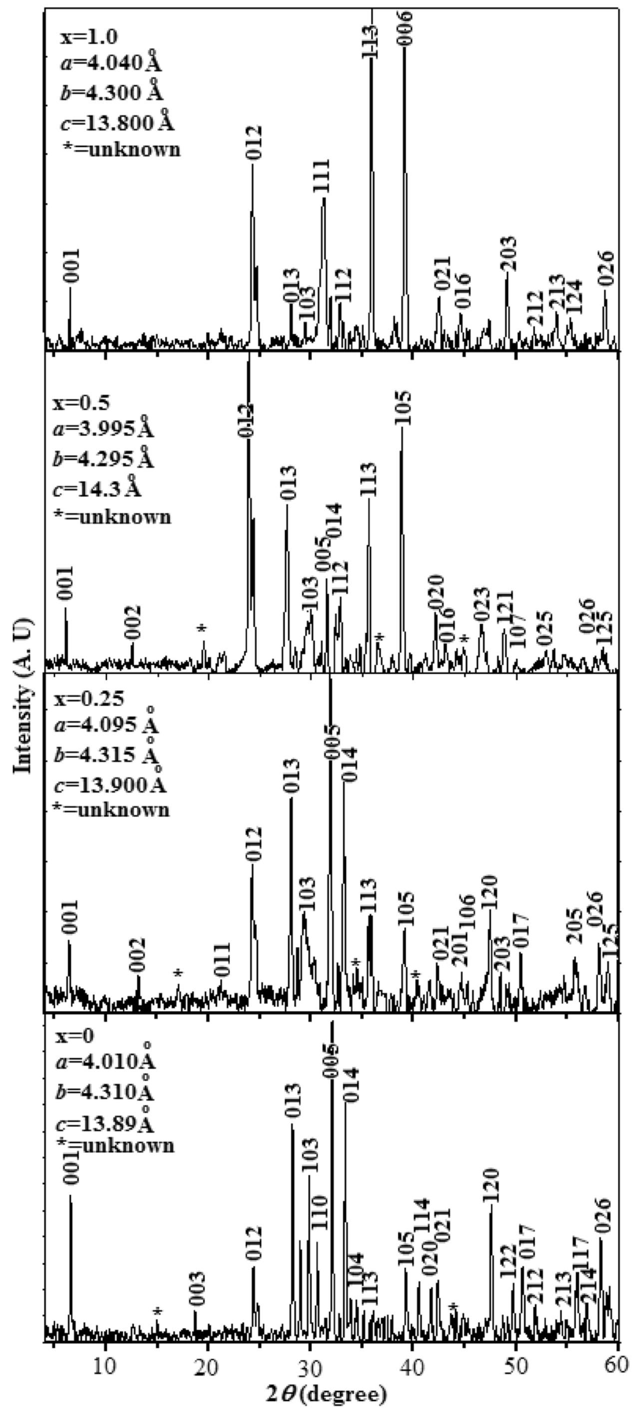

Fig. 1 XRD graphs of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 1.0) samples

orthorhombic crystal structure with PMMM space group. The *c*-axis length is marginally altered in all the doped samples and intensity of some peaks (012, 005 and 105) is systematically varied with the doping of Ti at the inter-plane sites. The systematic variation of the peaks' intensity and alteration in the *c*-axis length are finger prints of the incorporation of Ti at the Ca sites. The sample with x = 1.0 has shown smallest value for *c*-axis length (13.80 Å). This increase in the *c*-axis length of the sample with x = 0.5 may be attributed to the Jahn–Teller distortion [16, 17]. The *a*-axis and *b*-axis lengths are marginally altered.

In Fig. 2a, the variations of electrical resistivity versus temperature measurement for all the samples are shown. It is observed that, all the samples are found with metallic behavior in resistivity between room temperature and onset temperature of superconductivity. The transition regions of the resistivity versus temperature data for all the samples are shown in Fig. 2b. The onset temperature of superconductivity for the samples with x = 0, 0.25, 0.50, 0.75, 1.0 are around 111.32, 111.95, 111.39, 110.88, and 109.94 K, while zero resistivity critical temperatures are found around 94, 99, 97, 99 and 91 K, respectively. In the samples with x ranges from 0 to 0.75, the superconducting transition temperature is increased from 94 to 99 K. While the sample with x = 1.0 showed a decreased value of critical transition temperature i.e. 91 K.

Figure 3 represents the AC-susceptibility measurement for the as-prepared samples. The samples with x = 0, 0.25, 0.5 showed increased magnitude of diamagnetism in the in phase component of susceptibility χ′. The out of phase component is represented by χ″ which shows the power losses in the superconducting samples. However, for x > 0.5 a decreasing behavior is observed. The increased values of

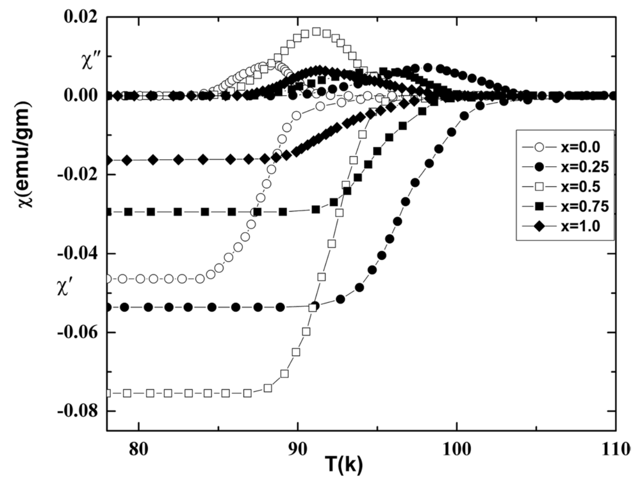

Fig. 3 AC-susceptibility versus temperature plots of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75,1.0) superconductive sample

T_c(R = 0) and magnitude of diamagnetism in the doped samples may be attributed to the improved inter-planar coupling caused by doping of smaller ionic size Ti atom which in turn by decreasing the distance among various CuO_2 planes, and hence enhanced the superconducting properties [18]. On the other hand suppression of these properties beyond certain doping level may be arising due to the difference in masses of Ti and Ca at the interplane sites [19].

The FTIR absorption measurements of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75,1.0) samples are shown in Fig. 4. The apical oxygen mode in CuTl superconductors consists of two types. For type-I Tl–O_A–Cu(2) mode, the observed range is

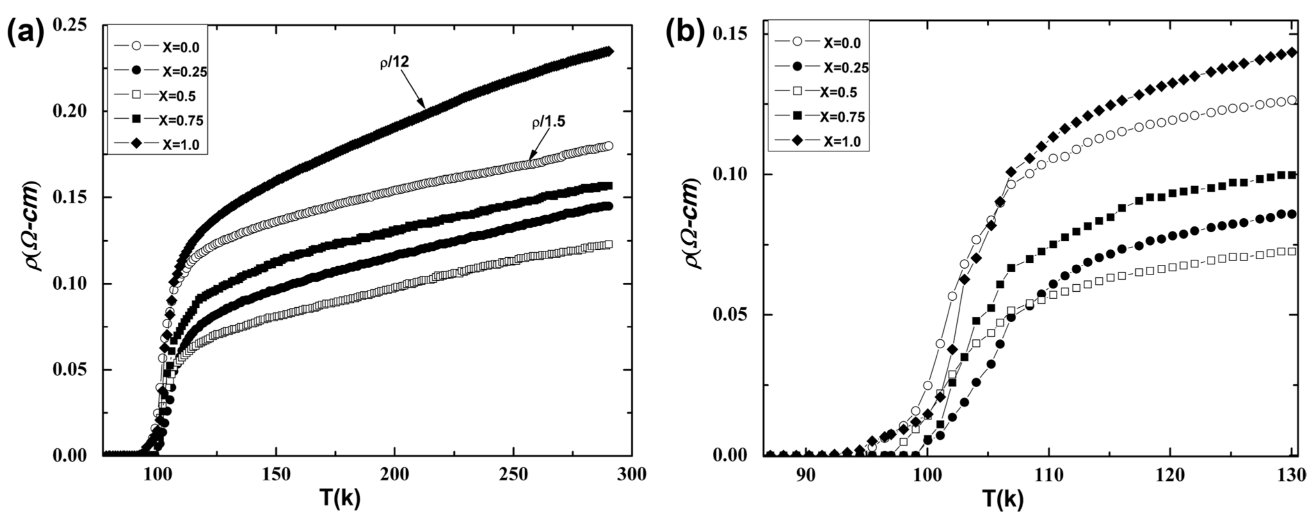

Fig. 2 **a** DC-electrical resistivity versus temperature graphs of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75,1.0) superconductors. **b** Transition region in the DC-electrical resistivity versus temperature graphs of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75,1.0) samples

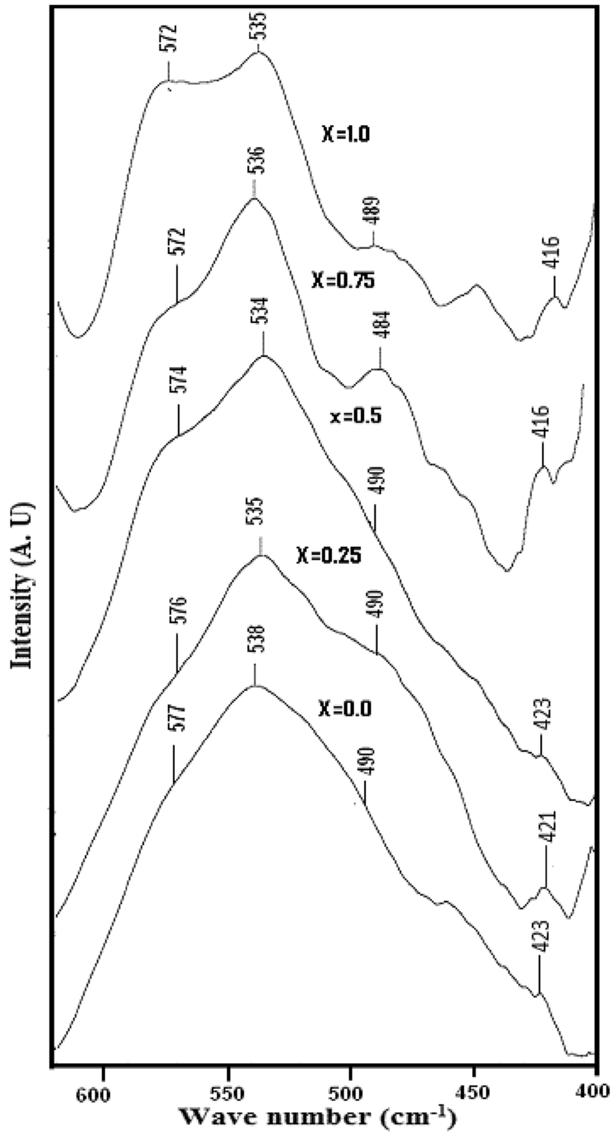

Fig. 4 FTIR absorption spectra of $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75,1.0) superconductors

400–480 cm^{-1}, while apical oxygen phonon mode of type-II Cu(1)–O_A–Cu(2) lies in the range of 480–540 cm^{-1} wave number. The planar oxygen mode exists around 540–600 cm^{-1} wave number range. The apical oxygen mode of type-I is softened from 423 (in the un-doped sample) to 416 cm^{-1} in the sample with x = 1. This softness shows an increased bond length of the apical oxygen which may be the reason for the elongation of the *c*-axis. The un-doped sample showed apical oxygen mode of type-II at 538 cm^{-1}. This mode is softened to 535 cm^{-1} with the doping of Ti content [19]. The high electro-negativity value of Ti (1.54 Pauling) as compared to Ca (1.0 Pauling) is the most possible reason for the softening of apical oxygen modes [18]. Planar oxygen modes are also softened and raised in intensity with increased Ti doping from 577 to 572 cm^{-1}. This softening in the planar oxygen phonon mode is attributed to the greater mass of Ti in comparison to Ca [9–11, 19]. The increased intensity of this mode shows that Ti has been substituted at the Ca interplane sites thereby decreasing the interplane distance and hence the improved interplane coupling.

4 Conclusion

To study the effect of smaller ionic size and higher mass atom on the superconducting properties, we have carried out the normal pressure synthesis of Ti-doped $(Cu_{0.5}Tl_{0.5})Ba_2(Ca_{2-x}Ti_x)Cu_3O_{10-\delta}$ (x = 0, 0.25, 0.50, 0.75,1.0) samples by two step solid-state reaction technique at 860 °C. All the samples showed orthorhombic crystal structure with PMMM space group. The *c*-axis length is increased in the sample with x = 0.5, while in the rest of the samples the lattice parameters are marginally altered. An increase in the critical transition temperature up to certain doping level (x = 0.75) and magnitude of diamagnetism (up to x = 0.5) is observed, which may be due to the improved inter-planar coupling brought about by the smaller sized Ti atoms. The suppression in the zero resistivity critical temperature (T_c) beyond x = 0.75 and magnitude of diamagnetism beyond x = 0.5 most likely appear due to the substitution of heavier Ti atoms at the lighter Ca sites. The Ti atoms of greater mass would generate anharmonic vibrations that are not favorable for optimum superconductivity.

In the FTIR absorption measurement, both the apical and planar oxygen modes are softened with increased doping of Ti, confirming the substitution of Ti at the Ca interplane sites because heavier atoms oscillate at lower frequency and hence lower wave number. From these studies we arrive at the conclusion that the smaller sized Ti atoms improve the interplane coupling and hence the superconducting properties up to certain doping level but on the other hand the Ti atoms are heavier than the Ca atoms thereby producing anharmonic oscillations i.e. the phonon associated with Ti are different than that of Ca that are not favorable for optimum superconductivity. Thus we say that the desired phonons' population is suppressed that results in suppression of the expected electron–phonon interactions and hence the superconducting properties. These studies strongly suggest the pivotal role of electron–phonon interactions in the mechanism of high temperature superconductivity.

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References

1. M. Karppinen, H. Yamauchi, Y. Morita, M. Kitabatake, T. Motosahi, R.S. Lu, J.M. Lee, J.M. Chen, J. Phys. Chem. Solids **177**, 1037 (2004)
2. H. Zhang, H. Sato, Phys. Rev. Lett. **70**, 1697 (1993)
3. J. Orenstein, A.J. Millis, Science **288**, 468 (2000)
4. T.H. Geballe, Science **259**, 1550 (1993)
5. C. Park, R.L. Synder, J. Am. Ceram. Soc. **78**, 3171 (1995)
6. M. Mumtaz, N. A. Khan, S. Khan, J. Appl. Phys. **107**, 103905 (2010)
7. N. A. Khan, J. Asim, A. A. Khurram, H. Naghma, Physica C **425**, 90 (2005)
8. N.A. Khan, M. Shamraiz, J. Phys. **439**, 012022 (2013)
9. N.A. Khan, M. Rahim, J. Alloy Compd. **481**, 81 (2009)
10. M. Rahim, N.A. Khan, J. Alloy Compd. **513**, 55 (2012)
11. N.A. Khan, A. Raza, J. Supercond. Novel Magn. **23**, 199 (2010)
12. J. Bardeen, L.N. Cooper, J.R. Schrieffer, Phys. Rev. **108**, 1175 (1957)
13. H. Ihara, A. Iyo, K. Tanaka, K. Tokiwa, K. Ishida, N. Terada, M. Tokumoto, Y. Sekita, T. Tsukamoto, T. Watanabe, M. Umeda, Physica C **282–287**, 1973 (1997)
14. M. Tinkham, *Introduction to Superconductivity*, 2nd edn. (McGraw-Hill, Inc., New York, 1996)
15. H. Ihara, A. Iyo, K. Tanaka, K. Tokiwa, N. Terada, M. Tokumoto, K. Ishida, M. Umeda, Adv. Supercond. **IX**, 277 (1996)
16. M.A. Halcrow, Chem. Soc. Rev. **42**, 1784 (2013)
17. T. Hashimoto, S. Ishibashi, K. Terakura, Phys. Rev. B **82**, 045124 (2010)
18. N. Hassan, N.A. Khan, Mater. Chem. Phys. **112**, 412 (2008)
19. N.A. Khan, M. Arif, Physica C **488**, 35 (2013)