Enhanced Interlayer Coupling of CuO$_2$ Planes Promote the Superconducting Properties of Cu$_{0.5}$Tl$_{0.5}$Ba$_{2}$Sr$_{2}$Ca$_{2}$Cu$_3$O$_{10-\delta}$ (Y=0, 0.15, 0.25) Samples

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Abstract

The CuTI-1223 superconducting samples, doping the Sr atom at Ba site, have been synthesized at 860°C pressure. The charge reservoir layer (CRL) of Cu$_{0.5}$Tl$_{0.5}$-1223 superconductor is modified by doping Sr atom. The decrease in c-axis length which is most probably due to smaller size of Sr atom as compared to Ba. The substitution of Sr atom at Ba is confirmed by the Fourier Transform Infrared Spectroscopy (FTIR). The critical temperatures i.e., Tc(R=0). Tc$^{max}$ are increased with the Sr content which shows that superconducting magnitude enhanced. The excess conductivity analysis has been done using Aslamazov-Larkin and Lawrence-Donaich models. The crossover temperatures i.e., TCR-3D=TG, T3D-2D and T2D-SWF and c-axis coherence length (\(\xi_0\)) are slanted to lower values. Moreover, the inter-plane coupling (\(J\)) increases due to decrease in c-axis length. From fluctuations induced conductivity, it is found that there is an inverse relationship between critical temperatures and coherence length.

Keywords: Cu$_{0.5}$Tl$_{0.5}$-1223; Synthesis; Sr substitution; X-ray diffraction; Excess conductivity

Introduction

The cup-rate intrinsic superconducting parameters are structure dependent. There are two parts i.e., i) MBa$_2$O$_7$ [M=Cu, Tl, Bi, Hg, C] a charge reservoir layer (CRL) and ii) conducting copper oxide planes nCuO$_2$ [1] of general unit cell in HTSC. In unit cell, the CRL provides the carriers (cooper pairs) to the cooper oxide planes and due to these carriers superconductivity exit [2-4].

Hence, the modification in CRL has a vital role in superconducting properties. In order to enhance the magnitude of superconductivity, numerous scientists have tried to modification in CRL [Co, Fe, Al] [5-7] and in CuO$_2$ planes [Zn, Ni] [8-10]. The increase in anisotropy and reduce in inter-plane coupling may be possible due to thicker CRL. Although, in periodic table, both atoms i.e., Sr and Ba lie in the same group but Sr atom is smaller in ionic radius (1.35 Å) as compared to Ba (1.35 Å). It is expected that dopant Sr atom would help to squeeze the CRL for enhanced interlayer coupling and hence improved the efficiency of CRL to the conducting CuO$_2$ planes. In contrast to the fixed Cu valence (\(^{\sim}\)=2+) in the Ti-bilayer cuprate superconductors, the average formal valence of Cu in the Ti-monolayer compounds TiBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+3}$ varies as (2+n−1)+. This characteristic is reflected in linear augmented-plane-wave band-structure results for the simplest n=1 member of this Ti-monolayer homologous series, TiBa$_2$CuO$_4$, where the filling (\(\sim\)=0.16) of the planar Cu(3d)-O(2p) \(\sigma^*\) band is reduced well below one-half. It is shown that the 50-50 Ba-La alloy is an appropriate “parent” compound for this n=1 phase since the half-filled-band condition is restored. For any member of this Ti-monolayer series, the optimal doping for high-temperature superconductivity should involve a combination of structural and chemical contributions.

Experimental Details

Synthesis

The superconducting samples Cu$_{0.5}$Tl$_{0.5}$Ba$_{2}$Sr$_{2}$Ca$_{2}$Cu$_3$O$_{10-\delta}$ (y=0, 0.15, 0.25) were synthesized by using the solid state reaction method. In first step, we prepared the Cu$_{0.5}$Ba$_{2}$Sr$_{2}$Ca$_{2}$Cu$_3$O$_{10-\delta}$ (y=0, 0.15, 0.25) by mixing the Ca(NO$_3$)$_2$, 4H$_2$O, Cu(CN)$_2$, SrCO$_3$ and Ba(NO$_3$)$_2$ as starting compounds. These compounds were thoroughly mixed for almost 2 hours in mortar and pestle. The chamber furnace at 860°C is used for heat treatment. After 24 hours continuously firing, the furnace was put off. Repeat the process under the same atmosphere.

In second step, well calculated amount of thallium oxide (TiO$_2$) was added in precursor material and thoroughly mixed. The material was pelletized and these pellets were sintered for nearly 10 min to get finally Cu$_{0.5}$Tl$_{0.5}$Ba$_{2}$Sr$_{2}$Ca$_{2}$Cu$_3$O$_{10-\delta}$ (y=0, 0.15, 0.25) samples.

Characterizations

To measure the resistivity, we used four-probe method was used. In this method, four uniformly spaced silver paste contacts were applied. The crystal structure of the material was determined by X-ray diffraction (XRD) measurements using Bruker diffractometer at X-ray wavelength of 1.5418 Å.

Results and Discussion

The crystal structure of Cu$_{0.5}$Tl$_{0.5}$Ba$_{2}$Sr$_{2}$Ca$_{2}$Cu$_3$O$_{10-\delta}$ where; y=0, 0.15 and 0.25 superconducting samples have been determined from the x-ray diffraction data, shown in Figure 1. The dimensions of unit cell were calculated from check cell. All the samples have orthorhombic structure with PMMM space group. It can be seen from Figure 1 that there is a slight shift in peak positions to higher 2 theta values with the increase of Sr content, which is most probably due to the decrease in the c-axis length of the unit cell. The overall contraction of the unit cell can be seen from the decrease of both a and c axis with the Sr content.
Due to smaller in size, Sr atom prompt such modifications in the unit cell.

The resistivity versus temperature measurements of Cu_{0.5}Tl_{0.5}(Ba_{2-y}Sr_{y})Ca_{2}Cu_{3}O_{10-δ} (y=0, 0.15, 0.25) superconducting samples are in Figure 3a and inset is shown the variation of ρ290 K(Ω⋅cm) versus Sr content. These samples have shown metallic behaviour from room temperature down to onset of superconductivity. From resistivity analysis, it is observed that these samples have shown Tc(onset) around 114.5, 116.3 and 116.3 K whereas Tc(R=0) at 90.26, 95.47 and 96.5 K respectively, shown in Figure 3b. The systematic increase of Tc (R=0) and with increasing Sr content is mostly suggested that the dopant Sr atom at Ba site in Tc(onset) Cu_{0.5}Tl_{0.5}Ba_{3}O_{10-δ} (CRL) promotes efficient transfer of the carriers to the conducting CuO2 planes and hence as a result, the aforementioned superconducting parameters enhanced. The room temperature resistivity ρ 290 K(Ω⋅cm) is systematically decreased with the Sr content which shows that dopant atom boosts an extra metallic trend in the final compound.

FTIR absorption measurements of Cu_{0.5}Tl_{0.5}Ba_{2-y}Sr_{y}Ca_{2}Cu_{3}O_{10-δ} (y=0, 0.15, 0.25) samples are shown in Figure 4. Three vibrational modes are witnessed around 613.4, 483.7 and 421.2 cm⁻¹ in un-doped sample. However, with Sr doping in CRL, the former two modes are related to apical oxygen atoms of nature Tl-Oₐ-Cu(2), Cu(1)-Oₐ-Cu(2) are softened from 483.7 to 482.0 cm⁻¹ and 421.2 to 415.1 cm⁻¹ whereas the third mode related to the planar oxygen atoms of nature Tl-Oₚ-Cu(2), Cu(1) are hardened from 613.4 to 623.4 cm⁻¹. The softening/hardening of the oxygen modes are most possibly related with the relaxation and compression of apical and planar bond lengths due to stresses and strains created after the doping of Sr atom at Ba site.

**Excess conductivity analysis (FIC) Cu_{0.5}Tl_{0.5}Ba_{2-y}Sr_{y}Ca_{2}Cu_{3}O_{10-δ} (y=0, 0.15 and 0.25) samples**

By fitting the experimental data of resistivity in theoretical models i.e., Aslamazov-Larkin and Lawrance-Donaich, the excess conductivity analyses is done in the temperature regime around Tc and beyond. According to Aslamsov Larkin (AL) model, the conductivity Δσ(T) is given by:

\[ Δσ_{AL} = C \]  
\[ Δ σ_{AL}^{3D} = C^{3D} - 0.5 \]  
\[ Δ σ_{AL}^{2D} = C^{2D} - 1.0 \]

![Figure 1: X-ray diffraction spectra of Cu_{0.5}Tl_{0.5}(Ba_{2-y}Sr_{y})Ca_{2}Cu_{3}O_{10-δ} superconductor with Y=0, 0.15, 0.25.](image)

![Figure 2: (a) Variation of c-axis length and volume of unit cell with Sr content; (b) Variation of a-axis and b-axis length with Sr content.](image)

![Figure 3: (a) Resistivity measurements of Cu_{0.5}Tl_{0.5}(Ba_{2-y}Sr_{y})Ca_{2}Cu_{3}O_{10-δ} superconductor with Y=0, 0.15, 0.25 as a function of temperature; (b): Variation of critical temperatures Vs Sr content.](image)
Where, C is dimensional exponent and its values vary with dimension of fluctuations i.e., 0, 1, 2 for 3D, 2D and 0D fluctuations respectively [11-13].

Moreover, \( \frac{8k_{B}T}{C} \) is the reduced temperature, \( T_{c} \) is usually referred as mean field critical temperature [14,15] and C is the fluctuation amplitude.

\[
C^{3D} = \frac{e^{2}}{32\hbar\xi^{2}(0)} \quad (3)
\]

\[
C^{2D} = \frac{e^{2}}{16\hbar d} \quad (4)
\]

Where, e, d and \( \xi(0) \) are electronic charge, inter-layer thickness and \( \xi(0) \) coherence length respectively. Since Loweren Donich is a modified form of Aslamsov-Larkin theory and it explained the fluctuations from 2D to 3D regimes. In the light of Loweren Donich model, the excess conductivity and cross over temperature is given below,

\[
\Delta\sigma = \rho_{n} - \rho / \rho_{n} \quad (14)
\]

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\[
\Delta\sigma = \rho_{n} - \rho / \rho_{n} \quad (14)
\]

The 2nd term, \( J \) i.e., inter layer coupling is related with \( J = \pi^{2}/4 \) [16-18] here \( \epsilon \) is reduced temperature. Excess conductivity \( \Delta\sigma \) is determined by the expression:

\[
\Delta\sigma = \rho_{n} - \rho / \rho_{n} \quad (14)
\]

Where, \( \rho \) is the resistivity measured experimentally and \( \rho_{n} \) is the extra-plotted normal state resistivity. The fluctuation induced conductivity analysis (FIC) has been done employing the above cited models (Aslamazov-Larkin and Lawrance-Donaich). The extracted superconducting parameters are given in Tables 1 and 2. The graphs are plotted between \( \ln(\Delta\sigma) \) and \( \ln(\epsilon) \) of \( Cu_{0.5}Ti_{1-y}Ba_{y}Sr_{0.5}Ca_{0.5}Cu_{3}O_{7+y/2} \) (\( y = 0, 0.15, 0.25 \)) samples are shown in Figures 5a-5c. It can be seen from Table 1 that all the crossover temperatures i.e., \( T_{c,1D} \), \( T_{c,2D} \), \( T_{c,3D} \) have been suppressed with the Sr doping which shows that there is an inverse correlation between the crossover temperatures and superconductivity transition temperatures (\( T_{c,0} \) and \( T_{c,onset} \)). The zero temperature coherence length, interlayer coupling strength, electron-phonon coupling parameter and critical magnetic field calculated from the excess conductivity analysis are given in Table 2. It is observed that the interlayer coupling strength has been increased with the increase of Sr in the charge reservoir layer (CRL).

The values of parameters such as \( B_{0}(T) \), \( B_{c1}(T) \), and \( J_{c}(0) \) are increased with the Sr content. These parameters appreciably depend on thermodynamic critical magnetic field \( B_{0} \) and it is related to the free energy difference at the interface of normal and superconducting electrons. So in our case, the dopant atom seems to support in the difference of free energy and as a result, these parameters increases.

The coherence length along the c-axis \( \xi(0) \) and the Fermi velocity \( v_{F} \) of superconducting carriers are decreased with Sr content in \( Cu_{0.5}Ti_{1-y}Ba_{y}Sr_{0.5}Ca_{0.5}Cu_{3}O_{7+y/2} \) unit cell. Since \( K_{F} = (32\pi N/V)^{1/3} \); \( [n=N/V] \), \( \xi(0) = h^{2}k_{F}/2m\Delta \) and \( v_{F} \). These parameters are dependent on density of carriers and doping of Sr atom, increases the density of carriers which suppresses the order parameter’s values. It confirms that Sr atom promote the efficiency of transfer the charge carriers to the \( CuO_{2} \) planes.

Conclusion

The present work has been resulted in the following conclusions as stated by the above study. Using solid state reaction method, the Sr-doped \( Cu_{0.5}Ti_{1-y}Ba_{y}Sr_{0.5}Ca_{0.5}Cu_{3}O_{7+y/2} \) (\( y = 0, 0.15, 0.25 \)) samples were synthesized at ambient pressure. The XRD analysis shows that samples have orthorhombic crystal structure. The fluctuation induced conductivity analysis (FIC) has been done employing the above cited models (Aslamazov-Larkin and Lawrance-Donaich). Three vibrational modes are witnessed around 613.4, 483.7 and 421.2 cm\(^{-1}\) in un-doped sample. However, with Sr doping in CRL, the former two modes are related to apical oxygen atoms of nature \( Ti-O_{x} \); \( Cu_{y} \); \( O_{z} \); \( Cu_{z} \). These parameters are increased from 613.4 to 623.4 cm\(^{-1}\) whereas the third mode related to planar oxygen atoms of nature \( Ti-O_{x} \); \( Cu_{y} \) are softened from 483.7 to 482.0 cm\(^{-1}\) and 421.2 to 415.1 cm\(^{-1}\) whereas the third mode related to planar oxygen atoms of nature \( Ti-O_{x} \); \( Cu_{y} \) are hardened from 613.4 to 623.4 cm\(^{-1}\). The substitution of Sr at Ba site in the charge reservoir layer decreases the lattice parameters including c-axis, as a result, promotes the enhanced interlayer coupling. The magnitude of the superconductivity is notably increased with the inclusion of Sr which shows that dopant Sr atom at Ba site in \( Cu_{0.5}Ti_{1-y}Ba_{y}O_{10-δ} \) (CRL) promotes efficiency of transfer the carriers to the conducting \( CuO_{2} \) planes.

Figure 4: FTIR spectra of \( Cu_{0.5}Ti_{1-y}Ba_{y}Sr_{0.5}Ca_{0.5}Cu_{3}O_{7+y/2} \) \( y = 0, 0.15, 0.25 \) samples.
Figure 5: Representative figure of the excess conductivity analysis of Cu$_{0.5}$Tl$_{0.5}$(Ba$_{2-y}$Sr$_y$)Ca$_2$Cu$_3$O$_{10-δ}$ (y=0, 0.15, 0.25) superconductors.
From FTIR analysis, it has been observed that the planar and apical phonon modes are hardening and softening respectively. The library of FTIR spectra available in this laboratory includes more than 9400 phonon modes are hardening and softening respectively. The library of FTIR spectra available in this laboratory includes more than 9400 phonon modes are hardening and softening respectively.

Table 1: Widths of critical, 3D, 2D and 0D fluctuation regions observed from fitting of the experimental data of Cu\textsubscript{0.5}Tl\textsubscript{0.5}Ba\textsubscript{2-YSrYCa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10-δ} (y=0, 0.15, 0.25).

| Sample | \(\xi_c(0)\) | J | NG | \(\lambda_{p.d}\) | Bc(0) | Bc1 | Bc2 | \(\kappa\) | Jc(0)\(\times 10^3\) | VF\(\times 10^{-12}\) |
|--------|------|---|---|--------|-------|-----|-----|-----|-------------|----------------|----------------|
| Y=0    | 1.78 | 0.049 | 0.22 | 1020.6 | 1.426 | 0.06 | 128.7 | 63.79 | 0.76 | 1.47 |
| Y=0.15 | 1.78 | 0.049 | 0.15 | 907.97 | 1.603 | 0.08 | 128.7 | 56.74 | 0.96 | 1.45 |
| Y=0.25 | 1.77 | 0.051 | 0.02 | 561.22 | 2.594 | 0.18 | 128.7 | 35.07 | 2.51 | 1.37 |

Table 2: Superconductivity parameters calculated from FIC analysis of Cu\textsubscript{0.5}Tl\textsubscript{0.5}Ba\textsubscript{2-YSrYCa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10-δ} (y=0, 0.15, 0.25).

| Sample | \(\xi_c(0)\) | J | NG | \(\lambda_{p.d}\) | Bc(0) | Bc1 | Bc2 | \(\kappa\) | Jc(0)\(\times 10^3\) | VF\(\times 10^{-12}\) |
|--------|------|---|---|--------|-------|-----|-----|-----|-------------|----------------|----------------|
| Y=0    | 1.78 | 0.049 | 0.22 | 1020.6 | 1.426 | 0.06 | 128.7 | 63.79 | 0.76 | 1.47 |
| Y=0.15 | 1.78 | 0.049 | 0.15 | 907.97 | 1.603 | 0.08 | 128.7 | 56.74 | 0.96 | 1.45 |
| Y=0.25 | 1.77 | 0.051 | 0.02 | 561.22 | 2.594 | 0.18 | 128.7 | 35.07 | 2.51 | 1.37 |

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