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Superconducting fluctuation and infrared absorption of Cd-substituted $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ ceramics

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Abstract

$Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ ($x=0$–0.4) ceramics were prepared using the conventional solid-state synthesis method to investigate the effects of Cd^{2+} substitutions on superconducting fluctuation behavior, SFB and structural properties of the Tl1212 derivatives. Electrical resistivity measurements showed all the samples exhibit metallic normal-state behavior with zero resistivity critical temperature, $T_{c\ zero}$ increasing from 40.0 K ($x=0$) to 76.4 K ($x=0.3$) before decreasing to 74.8 K ($x=0.4$) with increasing Cd^{2+}. FTIR analysis in conjunction with XRD results indicates improved inter-plane coupling that is evidenced in the form of decreased *c*-axis length and softening of the apical oxygen mode when Cd concentration was increased. In order to study the effect of Cd substitutions on SFB, excess conductivity analysis above T_c was performed using the Aslamazov–Larkin, AL model in conjunction with the Lawrence–Doniach, LD model. The results showed cross-over between two-dimensional, 2D to three-dimensional, 3D SFB transition for all the samples ($x=0.1$–0.4) with decreasing temperature. The highest transition temperature, $T_{2D\text{–}3D}$ was observed at $x=0.3$ which showed both the longest coherence length, $\xi_c(0)$ and the highest inter-plane coupling constant, J within the series. Our results suggest that the increase in J and lowering of anisotropy, γ resulted in enhancement of superconductivity in the compound.

Keywords: C. Electrical properties; C. Superconductivity; D. Oxide superconductors

1. Introduction

Thallium based superconductors are one of the largest family of high temperature superconductors, HTSC which were first discovered by Sheng and Hermann in 1988. Among Tl-based superconductors, $TlSr_2CaCu_2O_{7-\delta}$ (Tl1212) interest researchers as its electrical behavior can be tuned by elemental substitution [1,2] and its structure is isostructural to $Y_1Ba_2Cu_3O_{7-\delta}$ [3]. HTSCs, including Tl1212 show large anisotropy in their normal and superconducting-state properties. This large anisotropy promotes fluctuation in the order parameter owing to short coherence lengths along the *c*-axis, $\xi_c(0)$ during the transport processes.

It is known that, the short $\xi_c(0)$ gives large fluctuations effect in HTSCs which is easily observable. The resistivity curve is linear but bends down just above critical temperature, T_c due to increase in conductivity which is attributed to superconducting fluctuations. Superconducting fluctuations can be studied by excess conductivity analysis using the Aslamazov–Larkin (AL) model, which is used in conjunction with the Lawrence–Doniach (LD) model. The excess conductivity can be computed by subtracting the background normal state conductivity from measured conductivity i.e. [4]

$$\Delta\sigma = 1/\rho_{measured} - 1/\rho_{background} \quad (1)$$

where ρ is the resistivity. The AL model [5] states that, excess conductivity can be expressed as follows:

$$\Delta\sigma/\sigma_o = A\varepsilon^{-\lambda} \quad (2)$$

where σ_o is the conductivity at 300 K, ε is the reduced temperature and is given by the relation $\varepsilon = \ln(T/T_c^P)/T_c^P$ where T_c^P is the temperature of the peak obtained from the derivative of resistivity versus temperature curve. The AL temperature independent constant, A has two values, $e^2/16\sigma_o d$ and $e^2/32\sigma_o\xi_c(0)$ for two-dimensional (2D) and

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three-dimensional (3D), respectively. The value of critical exponents, λ for 3D region is 0.5 and for 2D region is 1.0 where the value of λ can be obtained from the slope of ln ($\Delta\sigma$) versus ln ε plot.

There has been a number of papers on superconducting fluctuation behavior, SFB for Tl1212 compound [6,7] which revealed effect of elemental substitutions on 2D to 3D SFB transition. Interestingly, the elemental substitutions also contribute to the changes in $T_{2D\text{–}3D}$ and $\xi_c(0)$ [6,7].

In relation to the above, several studies on infrared absorption in Tl-based cuprates [6,7] have suggested enhancement in CuO_2 interplane coupling as a result of elemental substitution. The softening of apical oxygen mode in conjunction with XRD results have indicated reduction in the distance between CuO_2 planes and consequently the increase in interplane coupling [6,7]. For Tl1212, this enhancement leads to longer $\xi_c(0)$ and consequently improved superconducting properties due to reduction in γ and increase in J [6,7].

On the other hand, elemental substitution of Cd^{2+} in cuprates HTSCs has been previously reported [8,9]. In Bi-based superconductors, substitution of a small amount Cd^{2+} at Ca site showed improvement in T_c and critical current density, J_c which indicates optimization of charge carriers [8]. However, so far, effect of Cd^{2+} substitution at Ca site in Tl1212 compound has not been reported. It is interesting to see if the changes brought about by Cd^{2+} substitution will affect SFB in the compound.

In present study, we report the effects of substitution of Cd at Ca site on superconductivity and SFB of $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ (x=0–0.4) ceramics. Excess conductivity analysis was performed using the AL model as a framework combined with LD model while FTIR absorption spectrum measurements are analyzed to investigate the changes in phonon modes.

2. Experimental procedure

The $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ ($x=0$, 0.1, 0.2, 0.3 and 0.4) samples were prepared from high purity oxides ($\geq$ 99.999%) via solid state reaction using appropriate amounts of powders of $SrCO_3$, Yb_2O_3, CaO, CuO, Fe_2O_3 and CdO. The oxides were mixed completely and ground using mortar and pestle. The powders were then heated twice for 24 h at 900 °C in a box furnace with intermediate grindings followed by furnace cooling. The precursor materials were then ground for an hour and thoroughly mixed with Tl_2O_3 and Bi_2O_3 as a final composition. The powders were then pressed into pellets by applying a pressure of 5 t and sintered at around 1000 °C in a tube furnace for 5 min in flowing oxygen followed by furnace cooling to room temperature. The resistivity of the samples was measured using the standard four-point-probe method between 40 and 300 K. Phase identification of the samples was carried out by the powder X-ray diffraction method using a Phillips X'pert Pro model PW3040 equipped with Cu-K_α radiation. The Fourier transform infrared, FTIR absorption measurements were done using a Nickolet TM 5700 spectrometer. The spectral resolution was 4 cm^{-1} and 200 scans for the background (KBr) and sample spectrums were taken.

3. Results and discussion

The powder X-Ray diffraction analyses shows the dominant phase in all these samples was Tl1212 with tetragonal unit cell (space group P4/mmm) accompanied by minor 1201 phases. The c lattice parameter (Table 1) showed a decreasing value with the increase of Cd^{2+} substitution. The reduction of c lattice was expected as the smaller ionic radius of Cd (0.97 Å) was substituted in place of the larger Ca^{2+} (0.99 Å). For this series, excess conductivity analysis was performed only on the $x=0.1$–0.4 samples which showed metallic normal-state behaviors. Electrical resistivity as a function of the temperature (Fig. 1) for $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ ($x=0.1$–0.4) samples showed $T_{c\ zero}$ increase from 40 K ($x=0$) (not shown) to 76.4 K ($x=0.3$). Further substitution of Cd however, caused $T_{c\ zero}$ to slightly drop to 74.8 K ($x=0.4$) (Table 1). All the samples showed metallic normal-state behaviors where the resistivity curves were shifted upwards indicating an increase of resistivity. For all the samples, T_{conset} is observed above 80 K indicating that the superconductivity is dominated by the 1212 phase. The 1201 phase has been previously reported with $T_{c\ onset}$ below 50 K [1].

The resistivity data in the metallic region for $x=0.1$–0.4 fitted to the linear relation $\rho=\alpha+\beta T$ are shown in Fig. 1. The insets in Fig. 1 show the curves of temperature dependence of the derivative of resistivity where the peak temperature was used to calculate ε. The graph of ln ($\Delta\sigma/\sigma_o$) versus ln ε was plotted for samples $x=0.1$–0.4 (Fig. 2). All the samples revealed 2D to 3D transition of SFB with lowering of temperature as reported for Tl1212 compound [6,7]. The highest value of $T_{2D\text{–}3D}$ of 91.4 K was observed for the $x=0.3$ sample (Table 2). From the values of $T_{2D\text{–}3D}$, the $\xi_c(0)$ can be calculated for polycrystalline samples using the LD equation below as given in Ref. [7]

$$T_{2D-3D}=T_c[1+(2\xi_c(0)/d)^2] \tag{3}$$

where d is the distance between superconducting layers of

Table 1

$T_{c\ onset}$, $T_{c\ zero}$, 1212:1201 phase ratio and lattice parameters of $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7\text{-}\delta}$.

Cd content (x)	$T_{c\ onset}$ (K) ± 0.1	$T_{c\ zero}$ (K) ± 0.1	1212 lattice parameters		1212:1201 phase ratio (vol%) ± 1
			a(Å)	c(Å)	
0	88.1	40.0	3.797(1)	12.126(3)	91:7
0.1	85.1	57.5	3.796(1)	12.121(5)	95:2
0.2	88.5	68.2	3.795(1)	12.118(5)	90:7
0.3	93.6	76.4	3.794(2)	12.116(6)	97:2
0.4	91.9	74.8	3.793(2)	12.111(6)	92:5

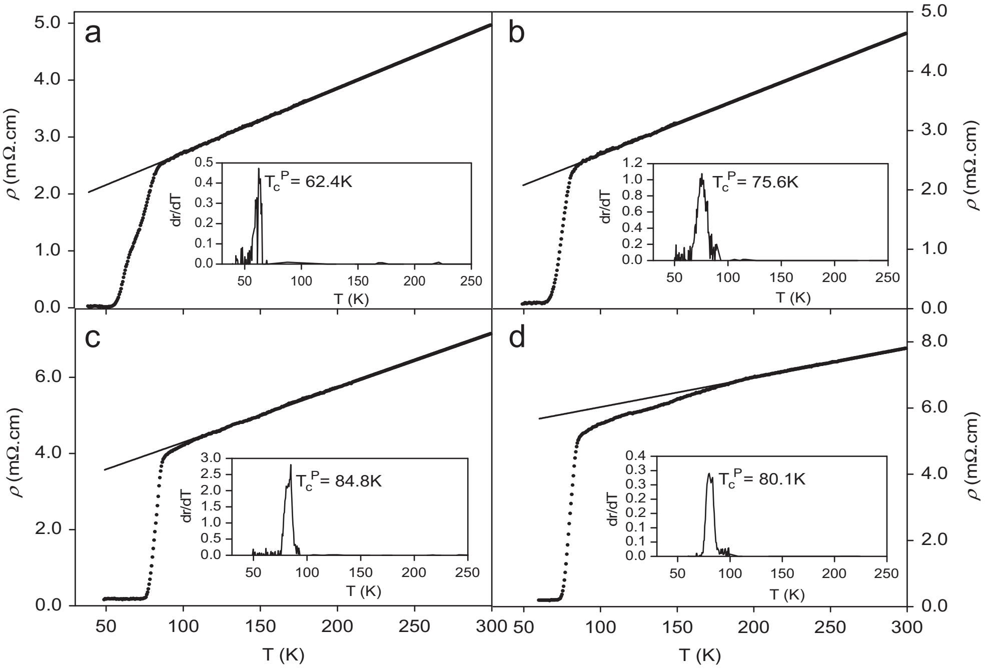

Fig. 1. Electrical resistivity of $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ for $x=0.1$–0.4 with the linear fit curves showing the background normal state resistivity projection. Inset shows plots of $d\rho/dT$ versus temperature. (a) x=0.1, (b) x=0.2, (c) x=0.3 and (d) x=0.4.

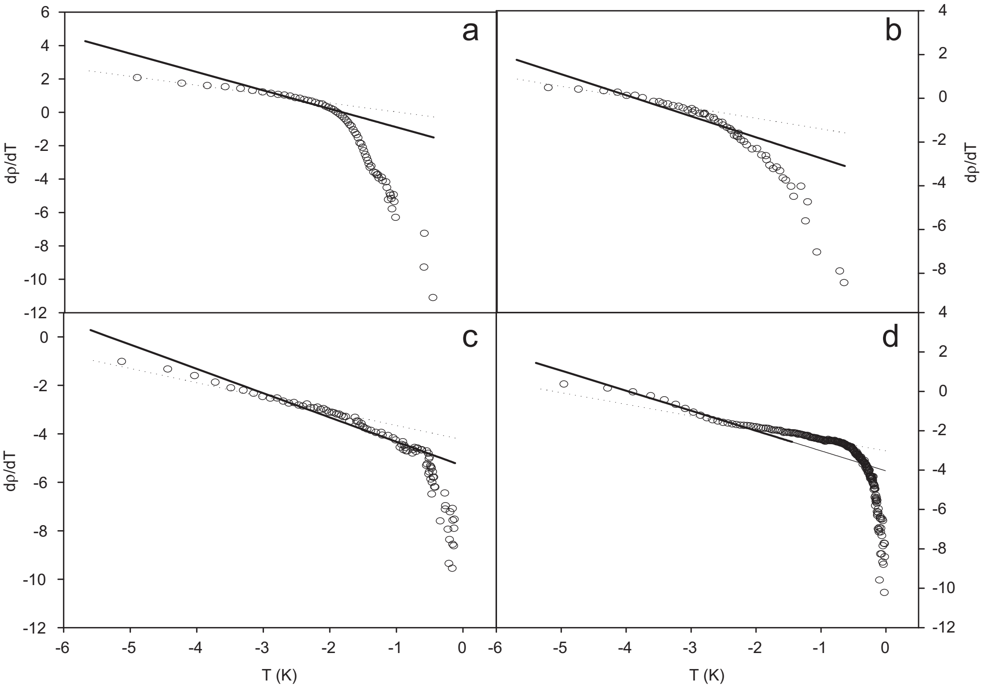

Fig. 2. Plot of ln $(\Delta\sigma/\sigma_o)$ vs. ln ε for $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ for $x=0.1$–0.4. The solid line represented 2D and the dotted line 3D theoretical slope, respectively. (a) x=0.1, (b) x=0.2, (c) x=0.3 and (d) x=0.4.

Tl1212 which is taken as 3.18 Å [10]. In addition, the concept of interlayer coupling, J based on Josephson coupling [7] as a result of $\xi_c(0)$ interaction with superconducting layers also was introduced by the LD model. The relationship between J and $\xi_c(0)$ is expressed by [7]

$$J=[2\xi_c(0)/d]^2 \tag{4}$$

Also, the anisotropy, γ [7] of layered superconducting system is given by

$$\gamma=\xi_{ab}(0)/\xi_c(0) \tag{5}$$

The value of $\xi_{ab}(0)\sim10$ Å reported for Y123 is used for this calculation as its isostructural to the Tl1212 system [3]. The computed values of $\xi_c(0)$, J and γ for all the samples

Table 2
Values of λ_{2D}, λ_{3D}, $T_{2D\text{–}3D}$, $\xi_c(0)$, γ and J for $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ superconductors.

(x)	(λ_{2D}) ± 0.001	(λ_{3D}) ± 0.001	$T_{2D\text{–}3D}$ (K) ± 0.1	ξ_c(Å) ± 0.001	γ ± 0.001	J ± 0.001
0.1	1.037	0.501	68.1	0.683	14.641	0.185
0.2	1.007	0.510	76.8	0.565	17.699	0.126
0.3	1.002	0.588	91.4	0.705	14.184	0.197
0.4	1.019	0.590	87.9	0.665	15.038	0.175

are tabulated in Table 2. The longest $\xi_c(0)$ within the series is 0.705 Å at $x=0.3$. The $x=0.3$ sample also showed the highest value of J(0.197) and the smallest value of γ(14.184). These results indicates that the Cd substitution modifies $\xi_c(0)$ and consequently increases the inter-layer coupling strength and reduces the anisotropy of the samples.

Fig. 3 shows FTIR absorption results for $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ ($x=0$–0.4) superconductors. For un-substituted ($x=0$) samples, the apical oxygen mode in the form of broad bands of types Cu–O(2)–Tl and Cu–O(2)–Bi/Tl were observed around 456 cm^{-1} and 540 cm^{-1}, respectively. Both of these modes were softened with the substitution of Cd where the Cu–O(2)–Bi/Tl was observed around 535, 534, 532, 530 cm^{-1} and Cu–O(2)–Tl was observed around 450, 449, 456 and 452 cm^{-1}. The FeO_2/CuO_2 planar oxygen mode in the Cd-free sample at around 587 cm^{-1}, however, was hardened with increasing Cd and was observed at 588, 589, 591 and 592 cm^{-1} (Fig. 3).

Cd substitution at Ca site is not expected to change the doping state of Tl1212 as both ions are divalent. A number of studies on Tl1212 reported optimization of holes concentration as a result of the substitution results in existence of maximum T_c [11]. In the present work, the increase in T_c and the less metallic normal state behavior may be due to differences in ionic radius of Cd and Ca that caused changes in internal cell pressure as a result of substitution. Our suggestion is similar to previous report on Mg^{2+} substitution at Ca^{2+} in $Tl_{0.5}Pb_{0.5}Sr_{1.8}Yb_{0.2}Ca_{1-y}Mg_yCu_2O_7$, which showed strong influence of ionic size effect on the variation of the T_c [7]. However, the reason for the slight drop in $T_{c\ zero}$ at $x=0.4$ is not clear. It may not be due to the percentage of 1212 phase as no large difference in 1212:1201 phase ratio was observed between $x=0.4$ and the rest of the samples.

Excess conductivity analyses of SFB of $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ ($x=0.1$–0.4) (Table 2) showed that Cd substitution influenced $T_{2D\text{–}3D}$, $\xi_c(0)$ and J. Interestingly, changes in $\xi_c(0)$ due to elemental substitution was also previously reported for other Tl1212 compound [6,7]. In the present work, the lowest anisotropy is observed owing to the highest $\xi_c(0)$ and J of the samples. In addition, the highest $\xi_c(0)$ and J possibly arise due to increase in carrier density (N/V) in conducting planes, where the reason is given in the light of our discussion on the FTIR analyses below.

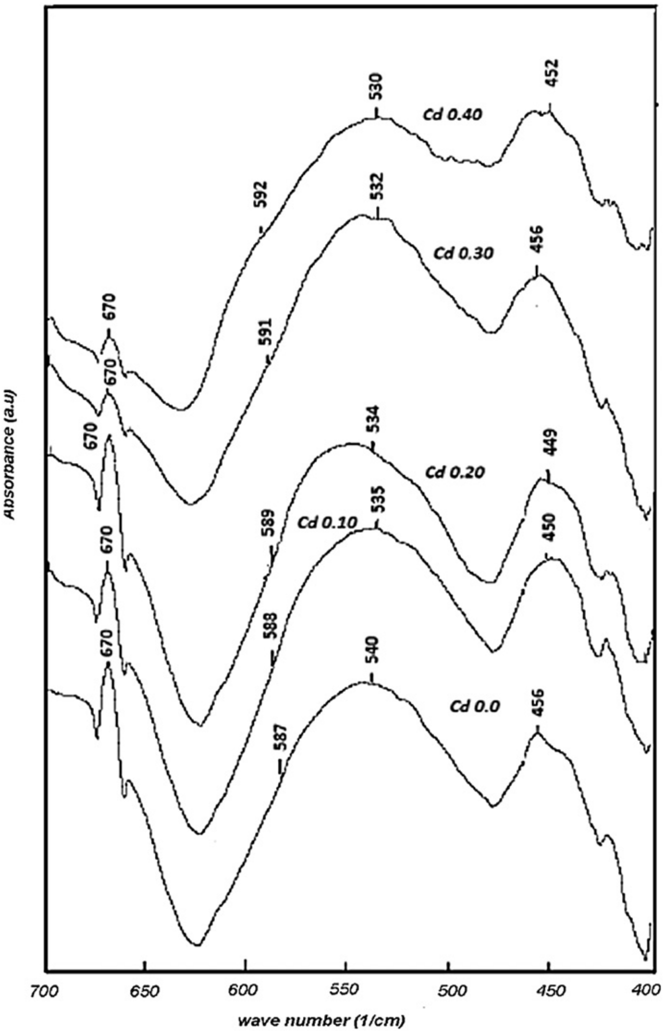

Fig. 3. FTIR absorption spectrum of $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_xCu_{1.99}Fe_{0.01}O_{7-\delta}$ ($x=0$–0.4).

The softening of apical oxygen mode as shown by FTIR results (Fig. 3) in conjunction with the decrease in c-axis length as observed from XRD data (Table 1) indicate increase in distance between Tl–O and CuO_2 plane with increasing Cd and an accompanying reduction in distance between CuO_2 planes consequently improving coupling between adjacent CuO_2 planes. This enhanced inter-plane coupling increased density of carriers in the conducting planes and would imply enhanced Fermi vector, $k_F=(3\pi^2\ N/V)^{1/3}$ and $\xi_c(0)(={}^{2}k_F/2\,m\Delta))$ [6,7]. This suggestion explains our results on excess conductivity analyses which revealed the highest $\xi_c(0)$ and J at $x=0.3$ as mentioned earlier. As such, the increased interplane couplings as a result of Cd substitution may be the reason for the variation in T_c values.

4. Conclusion

The effects of Cd substitutions at Ca site on SFB and structural properties of $Tl_{0.9}Bi_{0.1}Sr_{1.8}Yb_{0.2}Ca_{1-x}Cd_x Cu_{1.99}Fe_{0.01}O_{7-\delta}(x=0–0.4)$ ceramics have been investigated. Excess conductivity analyses using the AL model revealed 2D to 3D transition of SFB with the highest $T_{2D–3D}$ observed at $x=0.3$. The $x=0.3$ sample also showed the longest $\xi_c(0)$ and the highest J which was calculated using the LD model. FTIR analysis in conjunction with XRD results indicate that Cd-substitution enhanced the coupling of CuO_2 planes, which may be the reason for having the maximum $T_{c\ zero}$ value at $x=0.3$.

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