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Enhanced superconducting properties of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$ $Ba_2Ca_3Cu_4O_{12-\delta}$ ($y = 0, 0.15, 0.25, 0.35$) superconductor

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Abstract

The superconducting properties of $Cu_{0.5}(Tl_{0.5-y}Hg_y)Ba_2Ca_3Cu_4O_{12-\delta}$ compound have been studied by resistivity and AC magnetic susceptibility measurements. Mercury substitution has been found to improve the interlayer coupling in the unit cell of $Cu_{0.5}(Tl_{0.5-y}Hg_y)Ba_2Ca_3Cu_4O_{12-\delta}$ superconductor which is witnessed from the enhancement of superconducting properties like zero resistivity critical temperature, critical current density and flux pinning. The AC susceptibility measurements under different DC magnetic fields show that $Cu_{0.5}(Tl_{0.25}Hg_{0.25})$-1234 has superior flux pinning characteristics as compared to $Cu_{1-x}Tl_x$-1234 which make them useful for applications in external magnetic fields.

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Keywords: $Cu_{0.5}(Tl_{0.5-y}Hg_y)Ba_2Ca_3Cu_4O_{12-\delta}$ superconductor; Hg doping; Interlayer coupling; Post-annealing; Flux pinning; Critical current density

1. Introduction

The oxide superconductors in spite of their high critical temperature (T_c) suffer two main problems which limit their use in applications. One is their anisotropic nature and secondly, they are prepared in granular form for large-scale production [1–8]. The main source of anisotropy $\gamma = \xi_{ab}/\xi_c$ (ξ_{ab}, coherence length parallel to CuO_2 planes; ξ_c, coherence length normal to CuO_2 planes) in these materials is the charge reservoir block which separates conducting CuO_2 planes along *c* direction [9–11]. The transport of superconductor carriers along *c*-axis is found to depend largely on the nature and thickness of the charge reservoir layer. More insulating and thick charge reservoir layer acts as a potential barrier against the conduction of carriers in the direction normal to CuO_2 planes. The mean free path '*l*' of the carriers along *c*-axis decreases when they tunnel through this barrier that in turns increases the rate of collision between the carriers [12,13]. The wavefunction associated with the superconductor carriers are unsymmetrical and generate anharmonic processes that in turn degrades the superconducting properties like critical current density (J_c), flux pinning and critical field (H_c) [14]. On the other hand, the transport J_{ct} (intergrain critical current density) depends on the connectivity of the grains, weakly coupled grains lowers the transport critical current density of these materials.

In the homologous series of $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$, the $CuBa_2Ca_3Cu_4O_{12-\delta}$ (Cu-1234) superconductor is most promising due to its lower anisotropy ($\gamma = 1.6$) and high critical temperature T_c [15]. However, the normal pressure synthesis of this compound is not yet possible but the inclusion of thallium in the charge reservoir layer produces a new compound $Cu_{1-x}Tl_xBa_2Ca_3Cu_4O_{12-\delta}$ ($Cu_{1-x}Tl_x$-1234) which is a close derivative of Cu-1234 superconductor but its anisotropy is higher than that of Cu-1234 [16,17]. In the present studies, we have substituted Hg at Tl site in the charge reservoir layer and studied its effect on the superconducting properties of $Cu_{1-x}Tl_x$-1234. Mercury has smaller ionic radius (∼1.10 Å) as compared to thallium (∼1.40 Å). Hg due to its smaller ionic radius will reduce the thickness of the charge reservoir layer. The decrease in the thickness of the charge reservoir layer $Cu_{1-x}(Tl_{x-y}Hg_y)Ba_2O_{4-\delta}$ increases ξ_c of carriers and hence anisotropy of the final compound is decreased. The lowering of anisotropy will enhance the superconducting properties.

We also carried out post-annealing of $Cu_{1-x}(Tl_{x-y}Hg_y)$-1234 samples in oxygen atmosphere. Oxygen due to its very high electronegativity (3.5 Pauling's) controls the carrier concentration in

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CuO_2 planes of high T_c superconductors. The post-annealing in oxygen will possibly have two effects: (1) its doping to $Cu_{1-x}(Tl_{x-y}Hg_y)Ba_2O_{4-\delta}$ charge reservoir layer makes it more conducting and also increases carrier concentration in CuO_2 planes and (2) the diffusion of excess oxygen to grain boundaries increases the intergranular coupling [18–20].

2. Experimental

The $Cu_{0.5}Tl_{0.5-y}Hg_y-1234$ ($y=0$, 0.15, 0.25, 0.35) samples were prepared by solid state reaction method using $Ba(NO_3)_2$, $Ca(NO_3)_2$ and Cu(CN) as starting compounds. These compounds were mixed in appropriate ratios for about an hour in a quartz mortar and pestle and fired in a quartz boat at 860 °C for 24 h. The fired $Cu_{0.5}Ba_2Ca_3Cu_4O_{12-\delta}$ material was thoroughly mixed with Tl_2O_3 and HgO to give $Cu_{0.5}Tl_{0.5-y}Hg_yBa_2Ca_3Cu_4O_{12-\delta}$ ($y=0$, 0.15, 0.25, 0.35), as final reactants composition. Thallium and mercury mixed material was pelletized under 3.5 tonns/cm^2 pressure and enclosed in a gold capsule. The gold encapsulated pellets were sintered for 10 min at 860 °C followed by quenching to room temperature after the heat treatment. The superconducting phase identification was done by X-ray diffraction (XRD) measurements. The resistivity of the samples was measured by four-probe method and the bulk superconductivity by AC susceptibility measurements at a Lock-in frequency of 270 Hz. For infield AC susceptibility measurements, DC magnetic fields $H_{DC}=13$, 26, 41, 54 and 67 Oe were applied. The post-annealing of the samples was carried out in oxygen atmosphere in a tubular furnace at 550 °C for 6 h.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of $Cu_{0.5}(Tl_{0.25}Hg_{0.25})$-1234 superconductor. All of the diffraction lines are indexed according to tetragonal structure following space group *P4/mmm* with few unknown impurity peaks. The calculated *c*-axis parameters using these (*h k l*) is 17.529 Å smaller than that of $Cu_{1-x}Tl_x$-1234 superconductor [17], which shows that Hg substitution in $Cu_{0.5}(Tl_{0.25}Hg_{0.25})Ba_2O_{4-\delta}$ charge reservoir layer has decreased its thickness. The resistivity measurements of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y=0$, 0.15, 0.25, 0.35) samples are shown in Fig. 2. The zero resistivity critical temperature, $T_c(R=0)=105$ K in the sample without Hg is increased to 108 and 113 K in samples with $y=0.15$ and 0.25 but further increase of Hg ($y=0.35$) decreases $T_c(R=0)$ to 103 K. The

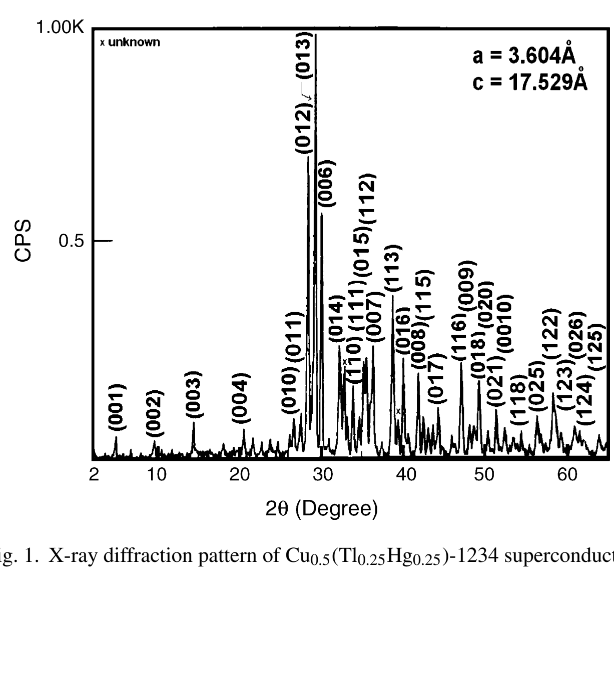

Fig. 1. X-ray diffraction pattern of $Cu_{0.5}(Tl_{0.25}Hg_{0.25})$-1234 superconductor.

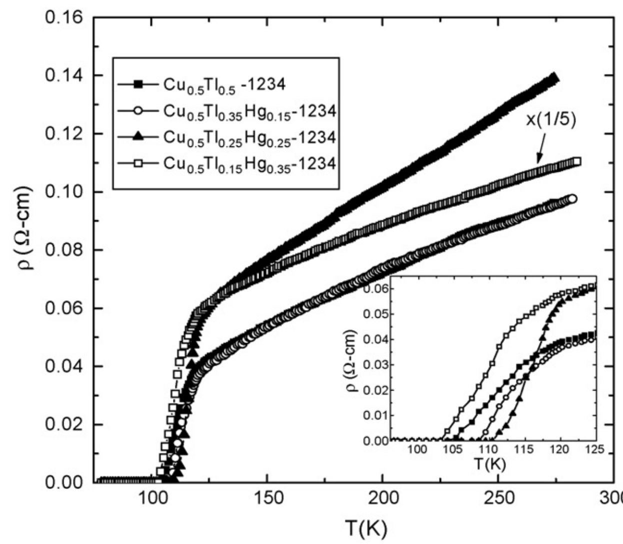

Fig. 2. Resistivity measurements vs. temperature of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y=0$, 0.15, 0.25, 0.35) superconductor.

variation of $T_c(R=0)$ with Hg content is plotted in Fig. 3. The mercury content, $y=0.25$ at which maximum zero resistivity critical temperature is achieved can be regarded as critical doping level above which the $T_c(R=0)$ starts decreasing in $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 superconductor. The decrease in the critical temperature is possibly due to the lowering of carrier concentration in CuO_2 planes from optimum (0.2/CuO_2 plane).

The AC susceptibility measurements of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y=0$, 0.15, 0.25, 0.35) samples are shown in Fig. 4. AC susceptibility technique is very important for the study of superconductivity in granular samples. The real part of susceptibility (shielding effect) 'χ'' gives the bulk susceptibility due to superconductivity within the grains or intergranular regions [7,21–23]. The suppression of superconductivity within the grains decreases the magnitude of χ'. On the other hand, the imaginary part 'χ''' of AC susceptibility is due to AC losses

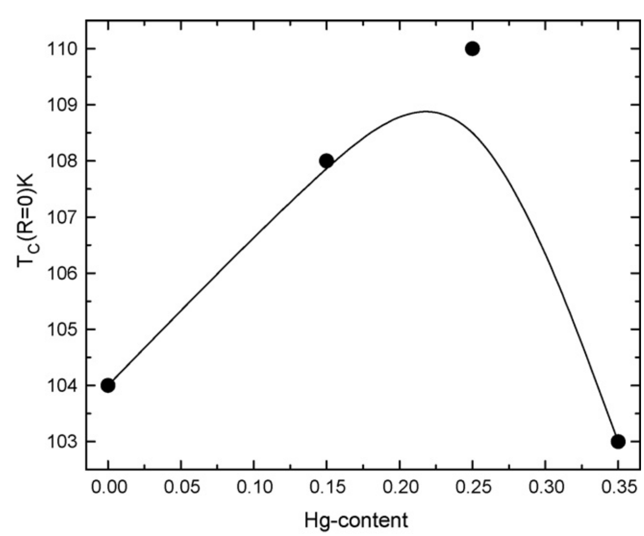

Fig. 3. Variation in $T_c(R=0)$ vs. Hg content of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y=0$, 0.15, 0.25, 0.35) superconductor.

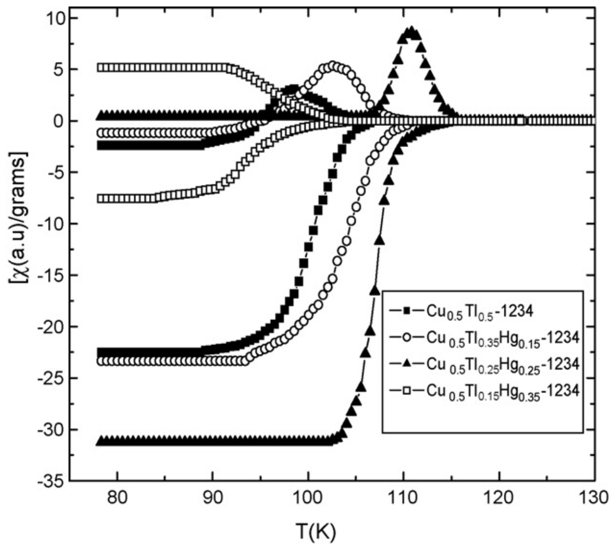

Fig. 4. AC-susceptibility measurements vs. temperature of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y = 0$, 0.15, 0.25, 0.35) superconductor.

corresponding to the flux penetration into the grains boundaries. This part of AC susceptibility provides information about the flux pinning and the nature of weak links between the grains [20,21]. It is observed from these measurements on $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 samples that there is an increase in critical temperature and the magnitude of diamagnetic signal with the increase of Hg concentration up to $y = 0.25$. These measurements indicate that the substitution of Hg increases the superconducting volume fraction of these samples. On the other hand, a very sharp χ'' peak is observed in the sample with $y = 0.25$ which suggest strong intergrain coupling, flux pinning and higher J_{ct} in this sample.

The *I–V* characteristics of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y = 0$, 0.15, 0.25, 0.35) samples are shown in Fig. 5. The critical current is increased by three times in the sample with $y = 0.25$. It is observed from above mentioned results that the sample with

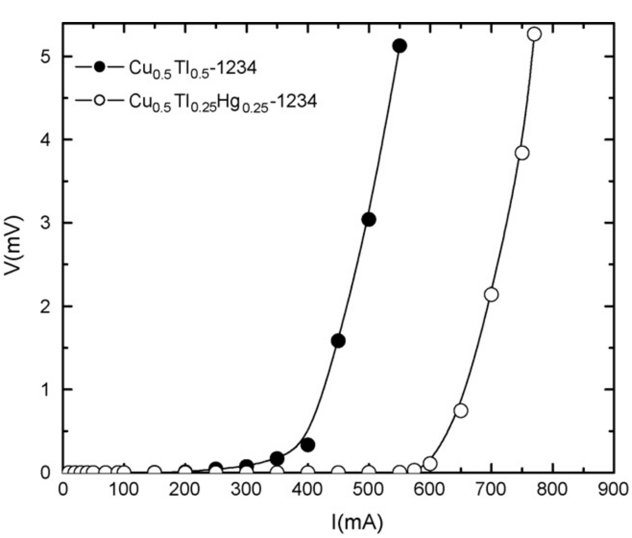

Fig. 5. *I–V* characteristics of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y = 0$, 0.25) superconductors ($H = 0$ G, $T = 77$ K).

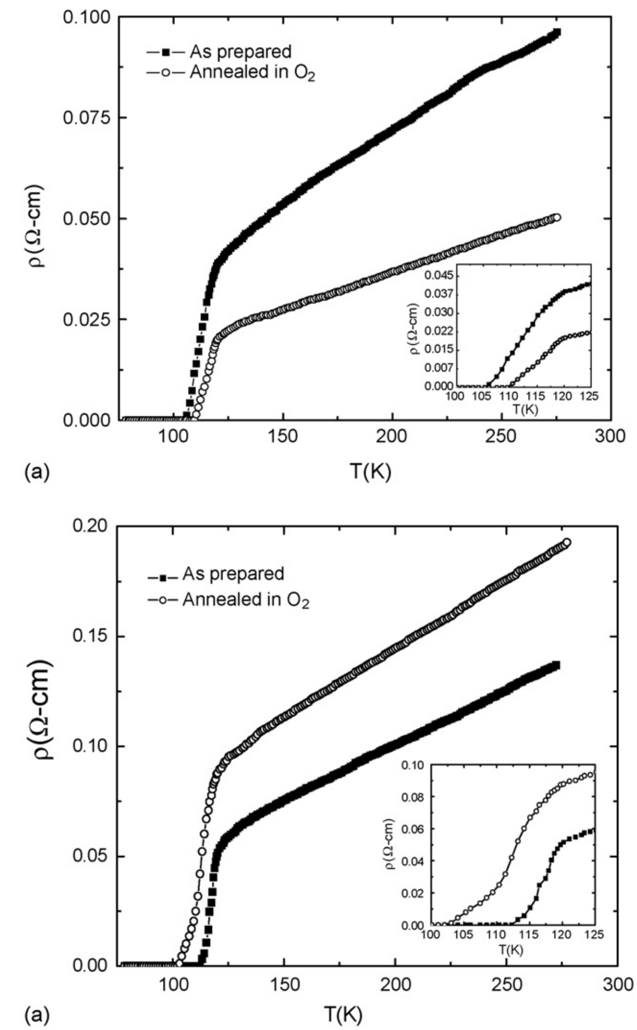

Fig. 6. Resistivity measurements vs. temperature of: (a) $Cu_{0.5}Tl_{0.5}$-1234 and (b) $Cu_{0.5}(Tl_{0.25}Hg_{0.25})$-1234 superconductors after post-annealing in oxygen.

$y = 0.25$ is best in terms of its higher $T_c(R = 0)$, T_P, and J_c, therefore, we have chosen this sample for post-annealing experiments in oxygen atmosphere and compared its results with the sample without mercury. In the following the results of post-annealing experiments are discussed.

3.1. Post-annealing in oxygen

In Fig. 6(a), the resistivity measurements of $Cu_{0.5}Tl_{0.5}$-1234 sample post-annealed in oxygen are shown. The *ρ–T* curve of the as-prepared sample is also included. It can be seen from this figure that there is an increase in $T_c(R = 0)$ from 104 to 109 K with a decrease in the normal state resistivity after post-annealing. But on the other hand, the post-annealing of $Cu_{0.5}Tl_{0.25}Hg_{0.25}$-1234 sample has decreased the critical temperature from 113 to 104 K along with the increase in room temperature resistivity, Fig. 6(b). These measurements suggested that as-prepared Hg free sample was in under-doped region and oxygen annealing has optimized the carrier concentration in this compound. However, the substitution of mercury in $Cu_{0.5}(Tl_{0.25}Hg_{0.25})Ba_2O_{4-\delta}$ charge reservoir layer promotes

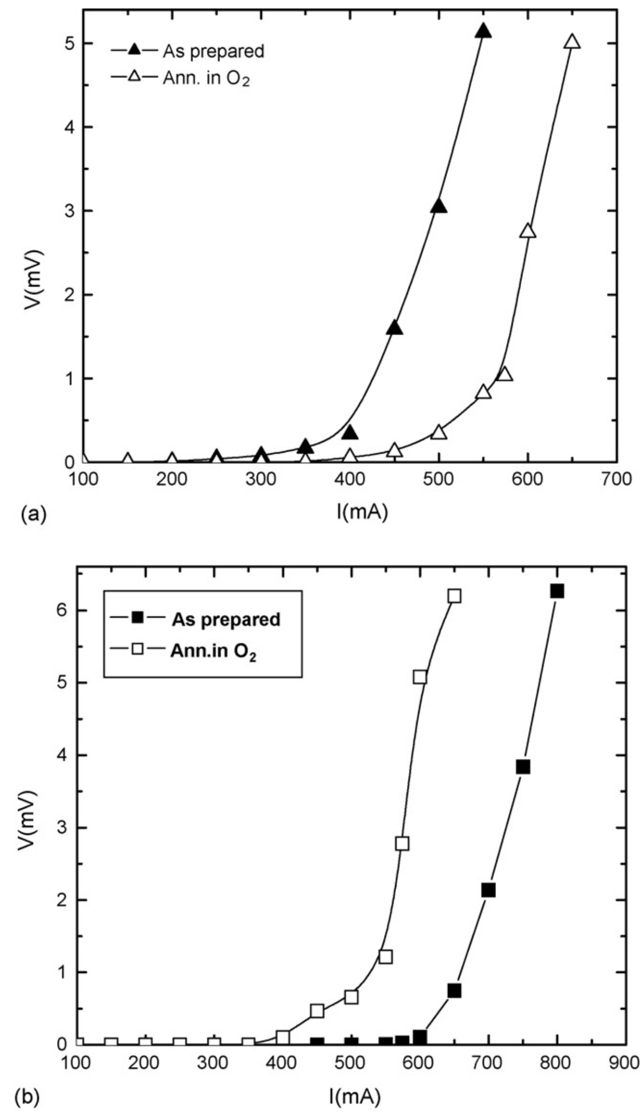

Fig. 7. *I–V* characteristics of: (a) $Cu_{0.5}Tl_{0.5}$-1234 and (b) $Cu_{0.5}(Tl_{0.25}Hg_{0.25})$-1234 superconductors ($H = 0$ G, $T = 77$ K) after post-annealing in oxygen.

the formation of material with optimum carriers in CuO_2 planes and after post-annealing in oxygen atmosphere the material become over-doped with carriers, therefore, zero resistivity critical temperature is decreased.

The critical current measurements of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y = 0$, 0.25) samples after post-annealing in oxygen are compared in Fig. 7(a and b). The critical current is increased in the sample with $y = 0$ but for the sample with $y = 0.25$ there is a decrease in critical current after post-annealing in oxygen. The increase/decrease of critical current density depends on the intrinsic properties of the material and on the connectivity of grains. In our case, the excess oxygen possibly has been incorporated both in grains and the intergranular sites. Presence of oxygen at grain boundaries increases the strength of intergrain coupling while within the grains it changes the intrinsic properties of the material. It can also be seen from Fig. 7(a and b) that the critical current of $Cu_{0.5}Tl_{0.25}Hg_{0.25}$-1234 sample after post-annealing is still higher than that of as-prepared $Cu_{0.5}Tl_{0.5}$-1234 sample, this could be due to the lower anisotropy of $Cu_{0.5}Tl_{0.25}Hg_{0.25}$-1234 superconductor.

3.2. AC susceptibility under DC magnetic field

The external magnetic fields can affect the physical properties (i.e. T_c, J_c) of high temperature superconductors; therefore, for the practical use of these compounds it is very important to study such properties in external magnetic fields. In this section, using AC susceptibility technique, we have studied the physical properties (i.e. intergranular coupling, flux pinning, etc.) of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234, $y = 0$ and 0.25 superconductors under various DC magnetic fields. We have done these experiments on as-prepared and oxygen annealed samples. The AC susceptibility measurements of these samples under external DC magnetic fields are shown in Figs. 8(a and b) and 9(a and b). The magnetic fields $H_{DC} = 13$, 26, 41, 54 and 67 Oe were applied to these samples parallel to AC magnetic field H_{AC} of the susceptometer

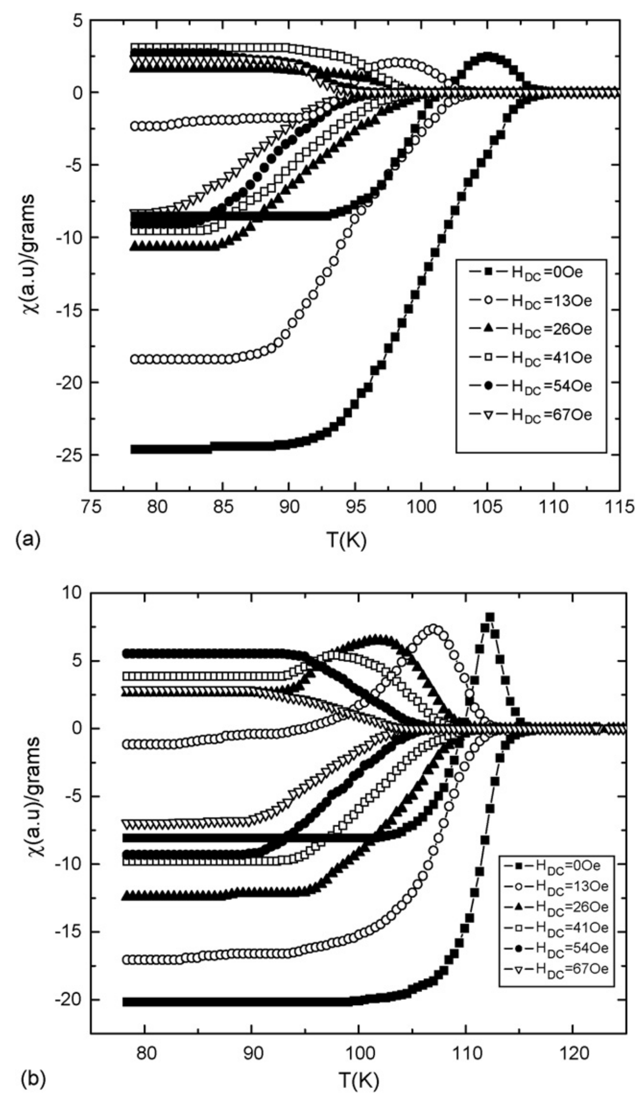

Fig. 8. AC susceptibility measurements of $Cu_{0.5}Tl_{0.5}$-1234 superconductor under external DC magnetic fields: (a) as-prepared and (b) post-annealed in oxygen.

coil. It is observed that with the increase of external DC magnetic field, the amplitude of in-phase component of magnetic susceptibility χ' is decreased and the onset of diamagnetism is shifted to lower temperatures. The width of out-of-phase component of magnetic susceptibility χ'' is increased while the peak position is shifted to lower temperature with the increase of H_{DC}. This peak appearing at a certain temperature T_P which is observed at 105, 98, 90, 90 and 85 K under $H_{DC} = 0$, 13, 26, 41 and 54 Oe for the as-prepared $Cu_{0.5}Tl_{0.5}$-1234 samples, Fig. 8(a) is associated with the coupling of grains and flux pinning. After post-annealing in oxygen atmosphere the peak temperature T_P and onset temperature of diamagnetism is increased to 112 and 116 K, respectively. A sharp diamagnetic transition and sharp peak in the out-of-phase component of susceptibility shows the improvement in the intergranular coupling after post-annealing in oxygen, Fig. 8(b).

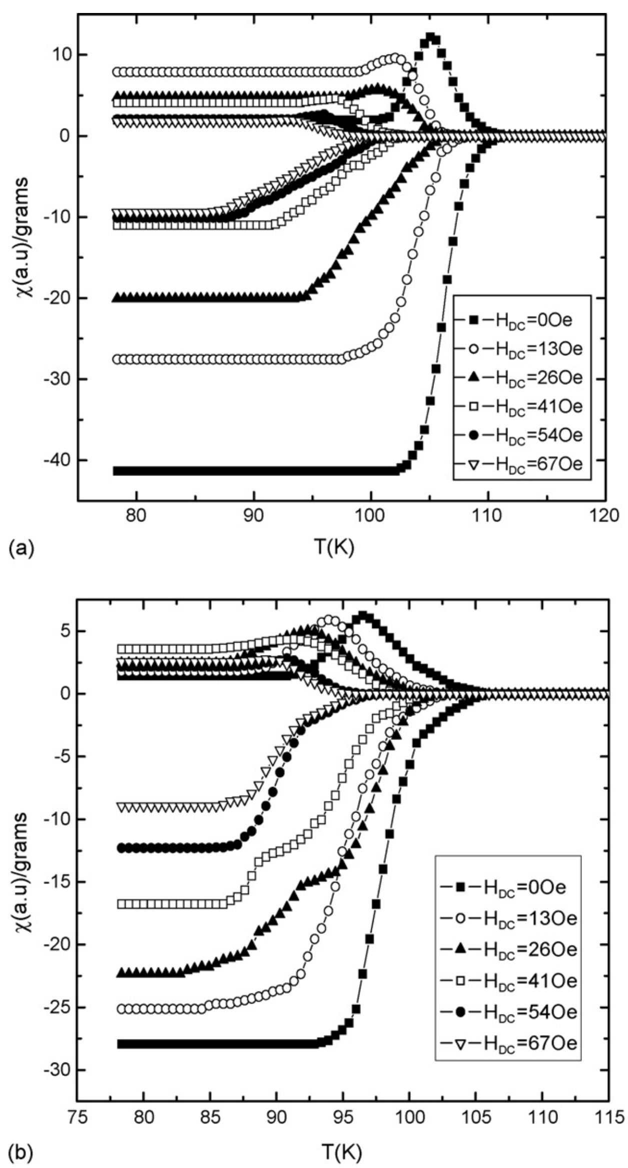

Fig. 9. AC susceptibility measurements of $Cu_{0.5}(Tl_{0.25}Hg_{0.25})$-1234 superconductor under external DC magnetic fields: (a) as-prepared and (b) post-annealed in oxygen.

Fig. 9(a and b) shows the AC susceptibility measurements of $Cu_{0.5}Tl_{0.25}Hg_{0.25}$-1234 superconductor under DC magnetic fields. As-prepared sample has sharp transitions in the in-phase and out-of-phase components of susceptibility. However, with the application of H_{DC} the magnitude of diamagnetic signal decreases and the peak in χ'' part of AC susceptibility is broadened and shifted to lower temperature, Fig. 9(a). The shift of χ'' towards lower temperature is associated with the energy loss ($q = \pi\chi'' B_o^2/\mu_o$) determined by the coupling of the grains [24]. On the other hand, post-annealing in oxygen atmosphere has decreased the superconductivity transition temperature and the peak temperature, T_P to 106 and 96.5 K, respectively. It is observed from susceptibility measurements under DC fields that magnitude of in-phase component of susceptibility is decreased with the appearance of two-step transitions when the filed is increased beyond 26 Oe. The appearance of second step in χ' part of susceptibility and shift of χ'' peak to lower temperature shows the decrease in the coupling of the grains. In Fig. 10(a and b), we have compared the shift of peak temperature with the increase of magnetic field for $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234; $y = 0$, 0.25 samples (as-prepared and post-annealed). It is observed from this figure that in the as-prepared $Cu_{0.5}Tl_{0.25}Hg_{0.25}$-1234 sample the shift of the peak temperature to lower values with applied magnetic field is small and the peaks are appeared at higher temperatures as compared to $Cu_{0.5}Tl_{0.5}$-1234 sample.

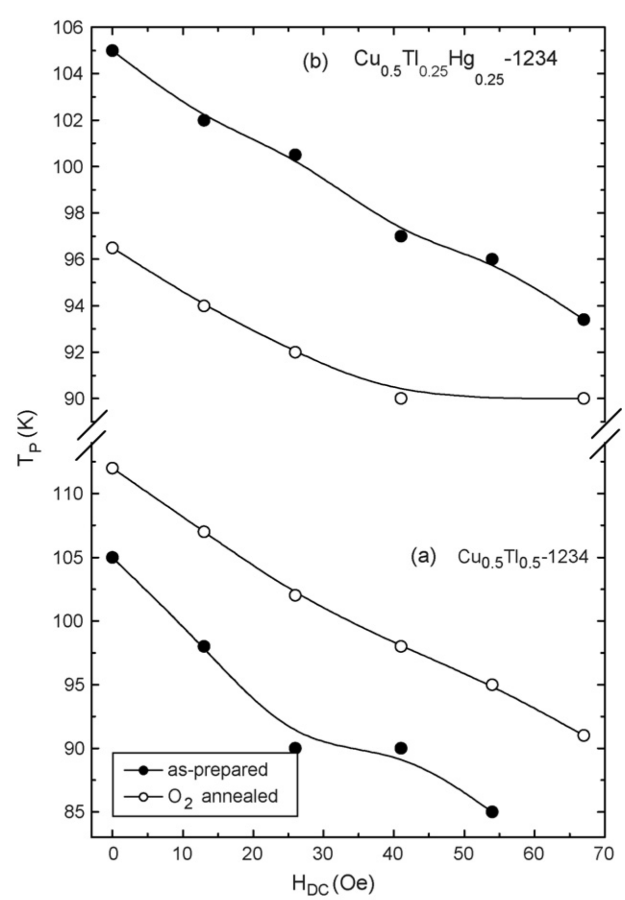

Fig. 10. The peak temperature 'T_P' of χ'' vs. H_{DC} of $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y = 0$, 0.25) superconductors: (a) $y = 0$ and (b) $y = 0.25$.

This behavior of T_P versus H_{DC} shows that the external magnetic field interact with the grains more strongly in Hg free samples due to their weaker inter-grain coupling and flux pinning; as a result the B_o penetrates deeper into the grains in these samples. Moreover, the lowering of anisotropy with the substation of Hg increases the flux pinning and critical current density of this compound. But after post-annealing in oxygen atmosphere the χ'' peaks are shifted to higher temperatures in Hg free sample but on the other hand, T_P is decreased in Hg substituted samples. However, the shift of T_P to lower temperatures with applied magnetic fields is still higher in Hg free samples, which shows that though oxygen annealing has improved the grain connectivity of $Cu_{0.5}Tl_{0.5}$-1234 sample but due to strong interlayer coupling (i.e. coupling between CuO_2 blocks) the flux pinning is stronger in Hg substituted samples.

4. Conclusions

We have synthesized $Cu_{0.5}(Tl_{0.5-y}Hg_y)$-1234 ($y = 0$, 0.15, 0.25, 0.35) superconductor samples. The Hg substitution in the charge reservoir layer has decreased its thickness and increased the coupling between the CuO_2 blocks. The strong interlayer coupling in these samples have enhanced their superconducting properties in terms of $T_c(R = 0)$, J_c, and flux pinning. The critical temperature and critical current density of $Cu_{0.5}Tl_{0.5}$-1234 samples is increased after post-annealing in oxygen, which shows that oxygen annealing has optimized the carrier concentration in CuO_2 planes and also increased the intergrain connectivity. In the case of $Cu_{0.5}Tl_{0.25}Hg_{0.25}$-1234 sample the critical temperature and critical current density is decreased after post-annealing in oxygen, which shows that excess oxygen is possibly doped within the grains but at the grain boundaries the oxygen content are not significantly changed. However, these samples have retained their strong flux pinning characteristics as observed from the AC susceptibility measurements under various DC magnetic fields.

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