

## Synthesis, X-ray data, and Hall effect measurements of Li-doped Tl-Ba-Ca-Cu-O superconductor

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Lithium-doped Tl-based superconductor was prepared by adding an amount of 0.3 mol.% to the  $\text{Tl}_{1.8}\text{Ba}_2\text{Ca}_{2.2}\text{Cu}_3\text{O}_x$  compound. The usual solid-state reaction method has been applied under optimum conditions. The x-ray data of the sample show a tetragonal structure with a high ratio of Tl-2223 superconducting phase. The sample showed a transition at 125 K and the zero resistance was observed at 117 K. Longitudinal (transport) and transverse (Hall) resistivities were measured at different temperatures under different magnetic fields and the data were interpreted. A positive Hall coefficient was observed at normal state and a sign reversal appears at temperatures lower than the critical temperature.

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### 1 Introduction

Among high-temperature superconductors (HTSs), Tl-based in the form of  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  (Tl-2212) and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (Tl-2223) have quite high critical temperature ( $T_c$ ) that ranges from 110 to 125 K. The grains of these superconductors grow preferentially in the a-b crystallographic directions leading to a high degree of structural anisotropy ( $c/a = 0.11-0.13$ ) [1, 2]. Samples of these compounds demonstrate texture and preferred orientation of their grains which is useful in the development of wires and tapes with improved links between the grains [3, 4]. Synthesis of these superconductors as single phases requires critical adjustments of the chemicals and the processing conditions [5, 6].

Doping with various elements was found to be useful and effective in improving the properties of HTSs. For example, Pb doping of Bi-Sr-Ca-Cu-O and Tl-Sr-Ca-Cu-O superconducting systems induces a partially melted liquid phase that eases the diffusion of the elements to form the high- $T_c$  phases and to increase their critical current ( $I_c$ ) [7, 8]. Li doping of Bi-based superconductors have been also studied [9-11]. Li doping reduces the melting and formation temperatures of the Bi-based superconductors leading to shorter annealing times. It was also found to be effective in increasing the critical temperatures and critical currents of both  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (Bi-2212) and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (Bi-2223) phases. Earlier, we have investigated the effect of Li doping on the properties of Tl-based superconductors [12]. We found that there is an optimum amount of Li addition at which the properties of Tl-based superconductor are enhanced. In this work, we analyze the structure and study the electrical properties of Li-doped Tl-based superconductor synthesized at the optimum conditions.

The unusual behavior of the Hall effect in many HTSs and in some conventional superconductors in the mixed and normal states has been a persistent problem in understanding the flux motion in superconductors. The sign reversal of the Hall angle below the critical temperature, as compared to the normal state, is in contrast to traditional models for the vortex Hall effect and is regarded as a fundamental problem of vortex

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dynamics. Experiments revealed that the Hall anomaly in HTSs observed in moderate magnetic fields, becomes more prominent in smaller magnetic fields and attains its maximum within the vortex liquid and thermodynamic fluctuation range [13, 14]. At temperatures higher than  $T_c$ , a rapid drop of the Hall resistivity precedes its sign reversal [15]. The occurrence of the Hall anomaly appears to be connected with the carrier concentration [16], being absent in heavily overdoped cuprates. In highly anisotropic HTS, like Bi-2212, a double sign reversal is observed [17] which is attributed to weak pinning in these cuprates. These observations raised the question of whether such single or double sign reversal could also exist in Li-doped Tl-based superconductor which is also highly anisotropic.

## 2 Experimental

In our previous work [12], we studied the effect of Li doping on the properties of Tl-based superconductors by adding different amounts of  $\text{Li}_2\text{CO}_3$  to the  $\text{Tl}_{1.8}\text{Ba}_2\text{Ca}_{2.2}\text{Cu}_3\text{O}_x$  compound. The highest  $T_c$  was observed after adding 1 wt% of  $\text{Li}_2\text{CO}_3$  to the previously mentioned compound. Therefore, we decided in this work to add 1 wt% of  $\text{Li}_2\text{CO}_3$  to obtain a sample of high quality.  $\text{Li}_2\text{CO}_3$  disassociates at temperatures lower than the annealing temperature of TBCCO and the 1 wt%  $\text{Li}_2\text{CO}_3$  quantity corresponds to 0.3 mol.% Li. The molar ratios of high purity oxides  $\text{Tl}_2\text{O}_3$ ,  $\text{BaO}_2$ ,  $\text{CaO}$ , and  $\text{CuO}$  were adjusted so as to obtain the Ca-rich stable high  $T_c$  phase,  $\text{Tl}_{1.8}\text{Ba}_2\text{Ca}_{2.2}\text{Cu}_3\text{O}_x$ . The solid-state reaction method was used to synthesize our samples. The oxides and  $\text{Li}_2\text{CO}_3$  were thoroughly mixed and ground using an agate mortar for 2 hours, and pressed into two disc-shaped pellets under about 30 MPa pressure. The pellets were wrapped in gold foil to prevent Tl loss during the synthesis and heated at 890 °C for 3 hours under oxygen flow and then furnace cooled to room temperature in 12 hours. Monolayer of the powder of the product was prepared on a glass plate and its x-ray diffraction pattern was obtained using a Philips powder diffractometer with  $\text{CuK}\alpha$  radiation at room temperature.

The samples were cut into the shape of rectangular plates of dimensions  $10 \times 8 \times 2.5 \text{ mm}^3$ . Using silver paste, we fixed four linear probes on the surface of one of the samples for transport resistivity measurements by the standard DC four-probe technique. Four point contacts were fixed on the top surface at the corners of the other sample for the Hall effect measurements by the van-der-Pauw technique. Each bulk sample and the connection leads were firmly fixed in a separate sample holder to avoid mechanical stresses during the measurements.

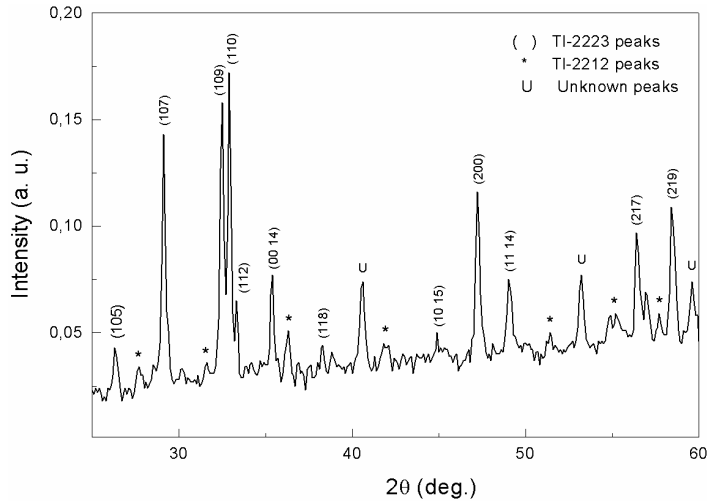
Lake Shore 7507 Hall-effect measurements system was used to measure the transport resistivity and Hall parameters at different temperatures. To measure the transport resistivity, 1 mA current was applied to the outer probes with a current source (Keithley 220) and the voltage drop through the inner probes was measured with a nanovoltmeter (Keithley 2182). Hall-effect data were collected using an IEEE computer interface and IDEAS software provided by Lake Shore. Cooling of the sample was achieved using a closed cycle cryostat (Advanced Research Systems) and Lake Shore 340 temperature controller. Measurements were done under magnetic fields up to 1.4 T, using a 7 inch variable gap electromagnet, applied perpendicular to the current direction.

## 3 Results and Discussion

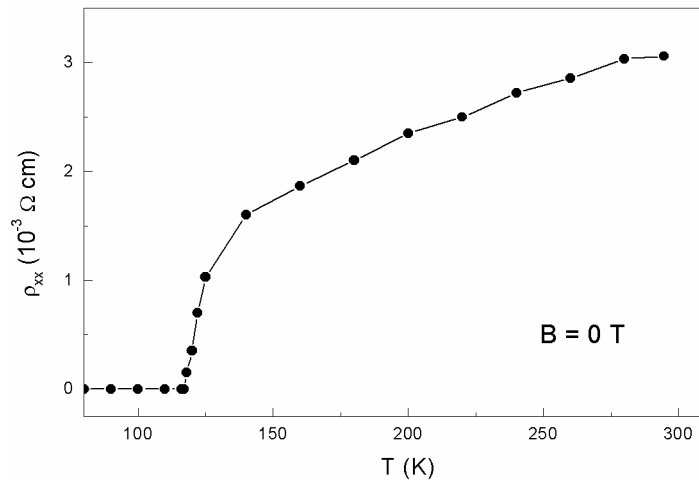
The x-ray diffraction pattern of the Li-doped Tl-based superconductor is shown in fig 1. The peak positions and intensities of the diffraction data reveals that our sample mainly consists of the Tl-2223 phase and a small amount of Tl-2212 as a minor phase together with some other unidentified peaks. Tl-2223 peaks are indexed and shown also in fig 1. The lattice parameters of the existing Tl-2223 and Tl-2212 phases in our sample were calculated from the d-values by a least square method and a computer program "x-ray". The results obtained were:  $a = 0.3851$ ,  $c = 3.5586 \text{ nm}$  and  $a = 0.3846$ ,  $c = 2.9255 \text{ nm}$ , respectively; showing a tetragonal crystal structure.

The transport resistivities  $\rho_{xx}$  at zero magnetic field were measured at different temperatures from 80 to 300 K and are shown in fig 2. Resistivity drops suddenly to zero near  $T_c$  showing a wide transition region with an offset  $T_c$  of 117 K and onset  $T_c$  of 125 K. The Hall resistivity  $\rho_{xy}$  was also measured at different temperatures in

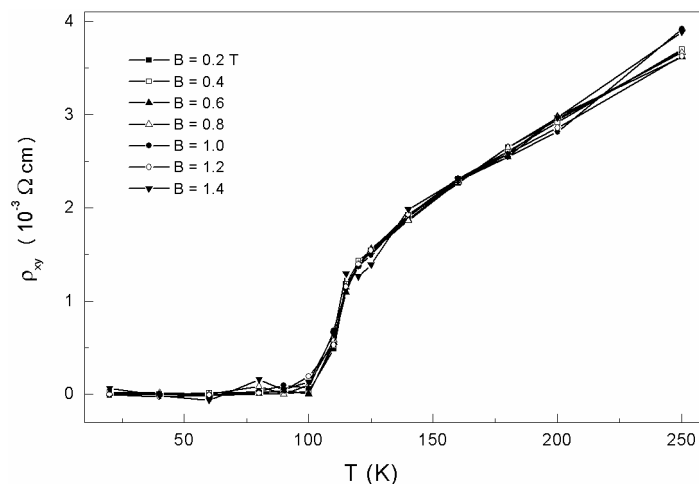
the range from 20 to 250 K under different applied magnetic fields up to 1.4 T. The representative curves are shown in fig 3. The  $\rho_{xy}$  versus T behavior is almost the same for all applied magnetic fields where  $\rho_{xy}$  drops to zero in a wide range from 125 to 100 K. This shows that  $\rho_{xy}$  is field independent especially at temperatures far lower than the room temperature.



**Fig. 1** XRD pattern of 0.3 mol.% Li-doped Tl-based superconducting sample.

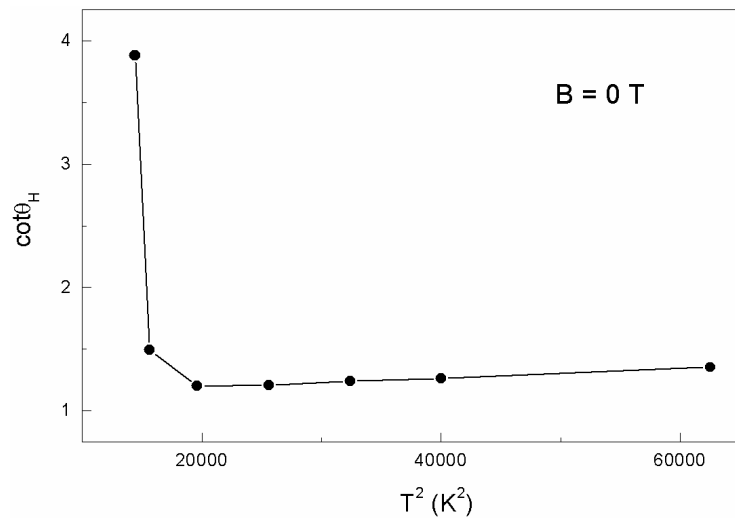


**Fig. 2** The temperature dependency of transport resistivity  $\rho_{xx}$  at zero applied magnetic field for Li-doped Tl-based superconductor.

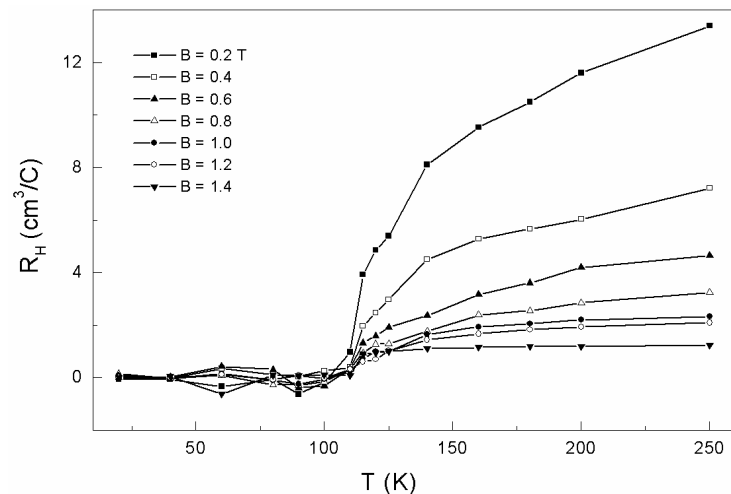


**Fig. 3** The temperature dependency of Hall resistivity  $\rho_{xy}$  at different applied magnetic fields up to 1.4 T for Li-doped Tl-based superconductor.

An interesting feature concerning the Hall effect of HTSs is the universal temperature dependence of the cotangent of the Hall angle ( $\cot\theta_H$ ) at temperatures higher than  $T_c$  [18, 19]. This behavior can be explained if two different scattering rates, a transport scattering time and a Hall (transverse) scattering time, are considered. The longitudinal resistivity ( $\rho_{xx}$ ) is determined by the transport scattering time and the Hall resistivity ( $\rho_{xy}$ ) is determined by both. The cotangent of the Hall angle ( $\cot\theta_H$ ) is defined as the ratio between the longitudinal resistivity ( $\rho_{xx}$ ) and the transverse resistivity ( $\rho_{xy}$ ). It was calculated at zero magnetic field and its  $T^2$  dependence is shown in fig 4. The transition from mixed to normal state may be observed from the sudden drop of  $\cot\theta_H$  from approximately 4 at temperatures below  $T_c$  to a value of 1.2 just after the transition temperature. After this, a weak  $T^2$  dependence was observed in the behavior of  $\cot\theta_H$  which is consistent with the observations in most HTSs [20].

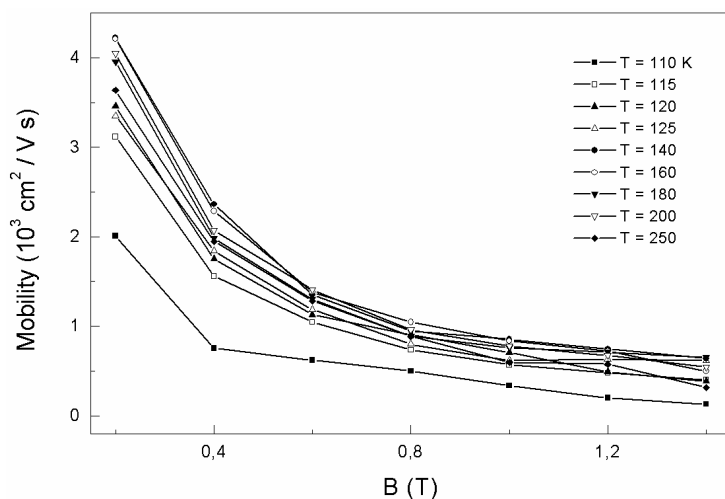


**Fig. 4** The  $T^2$  dependency of  $\cot\theta_H$  at zero applied magnetic field for Li-doped Tl-based superconductor.



**Fig. 5** The temperature dependency of  $R_H$  at different applied magnetic fields up to 1.4 T for Li-doped Tl-based superconductor.

The Hall coefficient  $R_H$  measured at different temperatures in the range 20-250 K under different applied magnetic fields up to 1.4 T is shown in fig 5.  $R_H$  is positive at the normal state (like many HTSs) indicating that conduction is done by hole-like and not electron-like carriers. Below  $T_c$  in the mixed state, some sign reversal (single or double) of  $R_H$  appears at temperatures between 40 and 100 K. The sign change was detected in many different HTSs [21, 22] and even in the newly discovered  $MgB_2$  superconductor [23]. The field dependencies of mobility at different temperatures from 110 to 250 K are shown in fig 6. Mobility decreases with increase of magnetic field at  $T = 110$  K. The same behavior was also observed at temperatures higher than  $T_c$  but higher values of mobility were measured.



**Fig. 6** The magnetic field dependency of mobility at different temperatures for Li-doped Tl-based superconductor.

## 4 Conclusions

Li-doped Tl-based HTS have been prepared under optimum conditions. The structure was tetragonal with high ratio of Tl-2223 superconducting phase and an offset  $T_c$  of 117 K. The Hall resistivity  $\rho_{xy}$  was found to be field independent especially at low temperatures.  $\cot\theta_H$  showed a weak  $T^2$  dependence and  $R_H$  is positive at the normal state. A sign reversal of  $R_H$  appears at temperatures lower than  $T_c$  under various magnetic fields.

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