Effect on Diamagnetism and Phonon Modes due to Mg and Be Doping at Ca Sites in $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_{3-y}\text{M}_y\text{Cu}_4\text{O}_{12-\delta}$ ($y = 0$ and 1.5 for $M = \text{Mg, Be}$) High Temperature Superconductors

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Abstract We synthesized as prepared and oxygen-annealed $\text{Cu}_{0.5}\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_{3-y}\text{M}_y\text{Cu}_4\text{O}_{12-\delta}$ ($y = 0$ and 1.5 for $M = \text{Mg, Be}$) High Temperature Superconductors (HTSCs) by using the solid state reaction method. It is observed that superconducting properties and the magnitude of the diamagnetism are enhanced by the doping of Mg and Be at the Ca site; this is due to smaller ionic sizes and higher electronegativities of Mg and Be as compared to Ca. Furthermore, interplanar coupling is also improved and shrinking of the axis length is the direct evidence of it. The carrier’s concentration in conducting planes is improved by carrying out post-annealing experiments in the oxygen atmosphere. Moreover, FTIR absorption measurements are also incorporated.

Keywords Diamagnetism · CuTl-1234 High Temperature superconductors · Enhanced superconductivity

1 Introduction

It was observed in previous studies that zero resistivity critical temperature [$T_c(R = 0)$] of $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_{3-y}\text{M}_y\text{Cu}_4\text{O}_{12-\delta}$ ($y = 0$) material was found to increase with the doping of Mg in the unit cell; for $y = 1.5$ [$T_c(R = 0)$] = 131 K was achieved which is hitherto highest in Cu-based superconductors. It is also observed from the convex shape of the resistivity versus temperature measurements that as-prepared material was in the region of carrier overdoping, and the number of carriers was optimized by postannealing experiments in air at 400 °C, 500 °C, and 600 °C. The $T_c(R = 0)$ was found to increase with postannealing and the best postannealing temperature was found to be 600 °C. The mechanism of increased $T_c(R = 0)$ is understood by carrying out infrared absorption measurements. It was observed through softening of the apical oxygen mode that improved interplane coupling was a possible source of enhancement of $T_c(R = 0)$ to 131 K [1]. In addition, by doping of Be at the Ca site in $\text{Cu}_{0.5}\text{K}_{0.25}\text{Tl}_{0.25}\text{Ba}_2\text{Ca}_{3-y}\text{Be}_y\text{Cu}_4\text{O}_{12-\delta}$ HTSC, it was reported by the analysis of fluctuation induced conductivity by doping of Be at Ca sites, the interplanar coupling is enhanced and FTIR analysis shows significant hardening of the Tl–O–Cu(2) modes, indicating a strong interaction between Be and Tl atoms. This interaction is most likely the reason for the smooth flow of charge along the c-axis of the unit cell, which could be a source of increased coherence length along the c-axis as well as an enhanced 3D character of fluctuations [2].

In this research, we doped Mg and Be at Ca sites of CuTl-1234 high temperature superconductors and achieved enhanced superconducting properties. The smaller ionic sized Mg and Be decreases the distance between the CuO2 planes and enhances the interplane couplings; also its diffusion at termination ends of grains increases the intergrain coupling. Shrinking of the axis length is the possible cause...
of enhanced interplanar coupling. It is also evident that by the doping of Mg and Be at the Ca sites in CuTl-1234 high temperature superconductors, zero resistivity critical temperature are enhanced. In addition, it is also found by the ac-susceptibility measurements that diamagnetism is enhanced by the doping of Mg and Be at the Ca site. The ac-susceptibility measurements have extensively been employed for probing the diamagnetism behavior [3–10]. The real part of ac-susceptibility ($\chi'$) tells about the intragrain magnitude of diamagnetism, whereas the imaginary part of ac-susceptibility ($\chi''$) gives the hysteresis losses associated with the intergrain weak links. The real part of $\chi'$–$T$ curve of a high $T_c$ sample gives an onset temperature of diamagnetism and the shielding fraction of the superconducting phases, whereas the imaginary part of $\chi''$–$T$ curve tells us about the flux dynamics and its penetration into the sample in the presence of a magnetic field. The mechanism of peak formation in $\chi''$ versus $T$ curves of the high $T_c$ samples has been nicely described in the literature [11–30].

2 Experimental

Samples were synthesized by the solid-state reaction method accomplished in two stages. At the first stage, Cu$_{0.5}$Ba$_2$Ca$_{1-y}$M$_y$Cu$_{4}$O$_{12-\delta}$ ($y = 0, 1.5; M = Be, Mg) was prepared using Cu(CN), Ba(NO$_3$)$_2$, Ca(NO$_3$)$_2$, MgO, BeO as the starting compounds. These compounds were mixed in appropriate ratios in an agate mortar and pestle. Thoroughly mixed materials were fired in air in a quartz boat at 880 °C for 24 hours followed by furnace cooling to room temperature. The precursor materials were then ground for about an hour and mixed with Tl$_2$O$_3$ (99%, Merck) to give Cu$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_{3-y}$M$_y$Cu$_{4}$O$_{12-\delta}$ ($y = 0$ and 1.5 for $M = Mg, Be$) as a final reactants composition. Thallium mixed material was then pelletized under 3.4 tons/cm$^2$ pressures and wrapped in a gold capsule. Pellet containing gold capsule was heat treated at 880 °C for 10 minutes and followed by quenching to room temperature after the heat treatment. The resistivity of the samples was measured by the four probe method. The rectangular bar shaped samples of dimensions 2 mm $\times$ 10 mm were used for resistivity measurements. The contacts are made by silver paste and constant current of 1 mA is passed through the sample during resistivity measurements in four probe method. The diamagnetism of the sample was measured by ac-susceptibility measurements at lock-in frequency of 270 Hz. In case of magnetic susceptibility, the real part of $\chi'$–$T$ curve of a high $T_c$ sample gives an onset temperature ($T_{\text{onset}}$) of diamagnetism; whereas the imaginary part of $\chi''$–$T$ curve tells $T_p$ where it gives the hysteresis losses associated with the intergrain weak links. The FTIR absorption measurements were done using Nicolet™ 5700 spectrometer. The measurements were carried out at the spectral resolution of 4 cm$^{-1}$. The background spectrum was taken with a KBr pellet. The sample was prepared by mixing 5 mg of the sample with 1 g of KBr, and the material was pelletized under 0.37 GPa pressure. The background and sample spectrum were taken by applying 200 scans. The superconductor phase was identified by XRD measurements, using CuK$\alpha$ radiation. The self-doping of the carriers was done by carrying out post-annealing of the samples in a tubular furnace in the flowing O$_2$ atmosphere at 550 °C for 5 hours.

3 Results and Discussion

3.1 As Prepared Cu$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_{3-y}M_y$Cu$_{4}$O$_{12-\delta}$ ($y = 0$ and 1.5 for $M = Mg, Be$) Samples

Figure 1 shows the X-ray diffraction scans of Cu$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_{3-y}M_y$Cu$_{4}$O$_{12-\delta}$ ($y = 0$ and 1.5 for $M = Mg, Be$) samples, prepared at 880 °C. Most of the diffraction lines are indexed according to tetragonal structure following the P4/mmm space group; the nominal derivative phases Cu$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_2$Cu$_2$O$_{10-\delta}$ and Cu$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_2$Cu$_1$O$_{10-\delta}$ are also marked in diffraction scans. It is observed that the length of the c-axis reduced with the doping of Mg and Be at Ca sites of CuTl-1234 superconductors. It is also noted that for these samples, there is no remarkable structural transformation with Mg and Be doping contents. It is also assumed from this data that the lattice parameter “c” of the samples is reduced monotonously with increasing Mg and Be concentrations due to the lower ionic size of Mg and Be as compared to Ca.

Figure 2a shows the resistivity measurements of as-prepared CuTl-1234. The critical temperature ($T_c(R = 0)$ of the as-prepared Cu$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_3$Cu$_4$O$_{12-\delta}$ (CuTl-1234) sample is 103.051 K, whereas 107.47 K for Mg doped and 112.274 K for Be doped samples. It is noted that every sample shows the linear temperature dependence characteristic of high temperature superconductors above the transition temperature. It is observed by viewing the figure regarding graphs of normal state resistivity $\rho_n$ at room temperature with $T_c$, that the $T_c$ has been enhanced by the doping of Mg and Be at Ca site of CuTl-1234 samples. This is due to the higher electronegativities of Mg and Be as compared to Ca. It is believed that the higher electronegativities of Mg and Be interacts more strongly with Tl as compared to Ca, thus introducing a strong interaction causing the shrinking of bond lengths. Since Tl in the charge reservoir layer plays a vital role in the flow of charge carriers to the conducting CuO$_2$ planes, the strong influence of the Mg and Be on the Tl some way promotes the smooth charge transfer between the charge reservoir layer and the conducting planes that is