Effect of MgO Nano-oxide Additions on the Superconductivity and Dielectric Properties of Cu$_{0.25}$Tl$_{0.75}$Ba$_2$Ca$_3$Cu$_4$O$_{12-\delta}$ Superconducting Phase

N.H. Mohammed

Abstract The effect of MgO nano-oxide on both superconducting and dielectric properties of polycrystalline (Cu$_{0.25}$Tl$_{0.75}$)-1234 was studied. The MgO-content varied from $x = 0.0$ up to $1.0$ wt$\%$ of the sample’s total mass. The volume fraction of the prepared samples ($x = 0.0, 0.2, 0.6$ and $1.0$ wt$\%$) was estimated from the room-temperature X-ray powder diffraction patterns. The superconducting transition temperature $T_c$, calculated from resistivity data, increased from 122 to 136 $K$ as $x$ increased from 0.0 to 0.8 wt$\%$ and then it decreased to 117 $K$ for $x = 1.0$ wt$\%$. Also, the dielectric properties of all samples were measured in the frequency range from 100 Hz to 4 MHz at different temperatures from 113 to 300 $K$. The real part of dielectric constant $\varepsilon'$ was strongly dependent on both temperature and frequency for all $x$ values. The imaginary part of dielectric constant $\varepsilon''$ and loss factor $\tan \delta$ showed dispersion which shift toward lower frequencies with decreasing temperature. The ac conductivity $\sigma_{ac}$ was derived from the admittance and sample dimensions in the same frequency range. It followed the power law $\sigma_{ac}(\omega) \sim \omega^{-\gamma}$ with $\gamma \approx 0.8$.

Keywords (Cu,Tl)-1234 • MgO nano-particles • Dielectric constants • Loss factor

1 Introduction

The crystal structure of (Cu$_{1-x}$Tl$_x$)-1234 superconducting phase is a tetragonal unit cell and it has four CuO$_2$-planes, acting as a conduction band, whereas the charge reservoir of (Cu$_{1-x}$Tl$_x$)-1234 is Cu$_{1-x}$Tl$_x$Ba$_2$O$_{4-\delta}$ [1]. (Cu$_{1-x}$Tl$_x$)-1234 superconducting phase was prepared by Ihara et al. [2] under a high pressure of 3.5 GPa and low pressure of 0.1 GPa at 950–1100 $^\circ$C for 1–3 hours in a gold capsule. They found that the superconducting transition temperature $T_c$ for this phase was higher than that of Cu-1234 and Tl-1234 by 8 $K$ and 4 $K$, respectively. Also, the anisotropy parameter for (Cu$_{1-x}$Tl$_x$)-1234 was found to be almost identical to that of Tl-1234 phase [3] and smaller than that of Cu-1234 [4]. Unfortunately, the high-pressure synthesis technique is not economical for practical applications. So, Khan et al. [1] reported a simple and direct method for (Cu$_{1-x}$Tl$_x$)-1234 synthesis at ambient pressure based on two steps of solid-state reaction technique. A single phase of (Cu$_{1-x}$Tl$_x$)-1234 was achieved at $T_c$ around 120 $K$ and zero resistivity temperature $T_0$ of about 106 $K$. The first chemical substitution in this phase was performed by Khan et al. [5], who substituted Be at Ca-site to improve the interplanar coupling. This study showed that Be-substitution at Ca-site contracted the lattice parameter c and the post-air annealing increased the oxygen content. Also, in a previous work, Mohammed et al. [6] had successfully synthesized Cu$_{0.25}$Tl$_{0.75}$Ba$_2$Ca$_3$-$_y$Er$_y$Cu$_4$O$_{12-\delta}$ superconducting phase by a single step of a solid-state reaction technique at ambient pressure and studied the effect of Er-substitution at Ca-site on its physical properties. It was found that the small content of Er ($0.0 \leq y \leq 0.05$) decreased the transition width and this result was attributed to the enhancement of volume fraction of this phase. Awad [7] studied the effect of MgO nano-oxide on the electrical and mechanical properties of Cu$_{0.25}$Tl$_{0.75}$Ba$_2$Ca$_3$Cu$_4$O$_{12-\delta}$ superconducting phase. He found that the lower concentration of MgO nano-addition to (Cu$_{0.25}$Tl$_{0.75}$)-1234 phase improved the critical current density $J_c$, enhanced both $T_c$ and the Vick-
ers microhardness and enhanced the volume fraction of the formed phase.

The high dielectric constant of high-temperature superconductors found numerous technological applications. Recently, materials with giant dielectric constant played an increasingly significant role in the growth of microelectronics because of the desire for smaller and more robust devices such as capacitors and memory devices [8]. In the case of memory devices based on capacitive components, such as static and dynamic random access memories, the static dielectric constant will ultimately decide the level of miniaturization [9]. The higher values of the dielectric constant were observed in many high-temperature superconductors [8, 10–20]. So with the advent of these HTSC compounds, the field of electronics had a great deal of potential in using this technology for a variety of applications. Relatively higher values of dielectric constants were reported for Bi2Ba2Nd1,6Ce0,4Cu3O10+δ [8], Tl2Ba2CaCu2O8−δ [10], Tl2Ba2Ca2Cu3O10−δ [10], Bi1.84Pb0.34Sr1.92Ca2.03Cu3.06In0.64O10+δ [11] and Cu0.5Tl0.5Ba2Ca2−xCdxCu3O10−δ [20] superconductors. Furthermore, Mumtaz et al. [21, 22] studied the dielectric properties of Cu0.5Tl0.5Ba2(Ca2−xMgx)5Oδ (Cu0.5Zn2.5)O10−δ and Cu0.5Tl0.5Ba2Ca3Cu4O12−δ bulk superconductors in the range of 10 KHz to 10 MHz and a negative capacitance (NC) phenomenon was observed. Also a similar phenomenon (NC) was observed by Cavdar in Tl2Ba2CaCu2O8−δ [10]. It is well known that there are four primary mechanisms of polarization in materials. Electronic polarization, atomic and ionic polarization, dipolar or oriental polarization and interfacial polarization, and each mechanism involves a short-range motion of charges and contribute to the total polarization of the material.

In this work, the effect of MgO nano-oxide additions on the superconductivity and dielectric properties of Cu0.25Tl0.75Ba2Ca3Cu4O12−δ superconducting phase was studied. The real and imaginary parts of dielectric constant ε′ and ε″, dielectric loss factor tan δ and ac conductivity σac for (MgO)xCu0.25Tl0.75Ba2Ca3Cu4O12−δ samples with x = 0.0 wt%, 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.0 wt% were calculated using the capacitance Cp, conductance G and admittance Y measurements in the frequency range of 100 Hz to 4 MHz and at different temperatures from 113 K to 300 K.

2 Experimental Technique

Samples with the nominal composition of Cu0.25Tl0.75Ba2Ca3Cu4O12−δ with different added amounts of nano-oxide MgO (0.0–1.0 wt%) were prepared by a single step solid-state reaction technique at ambient pressure. Amounts of Tl2O3, BaO2, CaO and CuO were used to prepare a sample of about 2.1 g with nominal compositions as 0.75:2:3:4:2.5. These compositions were ground in an agate mortar and then were sieved by a 65 μm sieve. After sieving, the nano-oxide MgO (40 nm, Sigma Aldrich) was added as a weight % to the sifted powder. The powder was pressed into a disc (diameter of 1.5 cm and thickness of about 0.3 cm), and then the disc was wrapped in a silver foil to minimize the thallium losses during the sintering process. The samples were heated in a sealed quartz tube (1.8 cm diameter and 12 cm long) at a rate of 2 °C/min to 780 °C, followed by a heating rate of 1 °C/min to 860 °C, and finally held at this temperature six hours. At the end of this period, the samples were slowly cooled to room temperature.

The samples were characterized by X-ray powder diffraction (XRD) using Shimadzu 7000 with CuKα-radiation (λ = 1.5418 Å) in the range 20° ≤ 2θ ≤ 60°. The grain size and homogeneity of the samples were identified using a Jeol scanning electron microscope JSM-5300, operated at 30 kV, with a resolution power of 4 nm. Energy dispersive spectroscopy (EDS) analysis were performed for the prepared samples using an Oxford X-ray micro-probe analysis connected to Jeol scanning microscope JSM-5300.

The electric resistivity of the prepared samples was measured by the conventional four-probe technique from room temperature down to T0 via a closed cryogenic system, employing helium gas as a working medium. The samples had the shape of parallelepipeds of approximate dimensions 1.5 × 0.2 × 0.3 cm3, and a conductive silver paint was used for the connections of copper leads with the sample. The temperature of the sample was monitored by a chromel versus Fe-Au thermocouple and stabilized with the aid of a temperature controller to within ±0.1 K. A typical excitation of 1 mA was used to avoid heating effects on the samples. The potential drop across the sample was measured using a Keithley 181 digital nano-voltmeter. The voltage was determined by taking the average of the values measured with the normal and reverse directions of applied current to eliminate the thermoelectric voltage of the junction leads.

The frequency dependent dielectric measurements were performed using Hioki-3532 LCR Hitester from f = 100 Hz to 4 MHz at different temperatures. Silver paint was painted in both sample surfaces and dried at room temperature. The sample is heated at 180 °C for one hour to ensure the good contact between silver metal and superconductor sample. Two copper leads were attached to the silver electrode surface to measure the capacitance. By measuring the capacitance Cp, conductance G and admittance Y for the prepared samples with different MgO nano-concentrations. The real and imaginary parts of dielectric constant ε′ and ε″, dielectric loss factor tan δ and ac conductivity σac of the dielectric samples were calculated using the following rela-