Improvement the superconducting parameters of Tl-1212 by Ruthenium substitution

R. Awad

Physics Department, Faculty of Science, Alexandria University, Alexandria, EGYPT.

Email: rawad64@yahoo.com

Abstract

Series of superconductor samples with a nominal composition of Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ with $0 < x > 0.3$ have been prepared via a solid-state reaction technique. The prepared samples have been characterized using x-ray powder diffraction (XRD) and scanning electron microscope (SEM). The tetragonal structure of Tl-1212 phase is not affected by Ruthenium-substitution whereas the lattice parameters a and c have been affected by this substitution. The electrical resistivity as well as the transport critical current density, for the prepared samples, is measured using a conventional four-probe technique. The superconducting transition temperature, $T_c$, enhances as $x$ increases from 0 to 0.05 and then it decreases, indicating that the Ruthenium improves the $T_c$ of Tl-1212 phase till $x = 0.05$. Also, the critical current, at 68 K without applied magnetic field, enhances from 75.23 A/cm$^2$ for $x = 0$ to 182.6 A/cm$^2$ for $x = 0.05$ and then it decreases to 35.21 A/cm$^2$ for $x = 0.15$. The electrical resistivity measurements for the samples with $x > 0.15$ show an anomalous behavior at temperatures around 120-180K, indicating the localization effect and the disorder of cations and oxygen.

1- Introduction

Recently, the effect of magnetic impurities on the high-temperature superconductors is one of interesting topics. It enhances the flux pinning energy, leading to enhancing the superconducting-transition temperature, $T_c$, and the critical current density, $J_c$ [1-3]. In Ti-cuprate, most of chemical substitutions are concerned with Ti-2223 for its high superconducting transition temperature and Ti-1223 for its potential use in industry. The chemical substitution in Ti-1212 is rare which may be due to its lower $T_c$ and $J_c$. The electrical resistivity, Hall effect and magnetoresistance measurements for Ti-1212 substituted by scandium were reported by Abou-Aly et al. [4] and Mohammed et al. [5]. Both the superconducting transition temperature and the hole-concentration were decreased as the Sc-content increased. An interesting result was obtained from the magnetoresistance measurement, for these samples, that is the critical current density was enhanced for lower Sc-content.

The crystal structures of Ti-1212, Ru-1212 and Y-123 are closer to each other. In Y-123 structure, the charge reservoir blocks contain chains of CuO$_4$ squares which in Ru-1212 are replaced by coron-sharing RuO$_6$ octahedral forming planar sheets. For Ti-1212, the $Y^{3+}$ ions replacing the Ca$^{2+}$ ions in the conduction-slabs and copper oxide replacing thallium oxide in the charge reservoir blocks. Both Ti-1212 and Ru-1212 have been described by a tetragonal unit cell with space group of P4/mmm. The first chemical substitution by Ruthenium in the superconducting cuprate was done by Xiong et al. [6] in La$_{1.85}$Sr$_{0.15}$CuO$_4$ system. They found that Ru- substitution in Cu introduced disorder in the system and the hole-filling mechanism, played an important role for the superconductivity suppression. Sader
et al. [7] studied the substitution of Cu$^{2+}$ ions RuSr$_2$GdCu$_2$O$_8$. They found that the ferromagnetic temperature, T$_{\text{m}}$, slightly depressed and superconducting transition temperature dramatically changed. This means that the RuO$_2$-layers are responsible for ferromagnetic transition and CuO$_2$-layers are responsible for the superconducting transition. Dong et al. [8] reported the effect of Ru on La$_{1.85-2x}$Sr$_{2x+0.15}$Cu$_{1-x}$Ru$_x$O$_{2z}$ and La$_{1.85}$Sr$_{0.15}$Cu$_{1-x}$Ru$_x$O$_8$ systems. The results showed that the lattice parameter a increased with increasing Ru-content while lattice parameter c and c/a decreased. The electrical resistivity data, for these systems, displayed that the superconducting transition temperature strongly suppressed and the critical content $x_c$, at which the superconductivity disappeared, for the two systems are 0.0225 and 0.019, respectively.

Due to the similarity between the crystal structure of Tl-1212 and Ru-1212, the partial replacement of Tl$^{3+}$ ions by Ru$^{4+}$ ions is reported in this work. Superconducting samples of type Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ with 0 < $x$ < 0.3 are prepared via a solid-state reaction technique and they are characterized using XRD, SEM, electrical resistivity and transport critical current density.

### 2- Experimental technique.

Samples with the nominal composition of Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ ($x$ = 0.0, 0.025, 0.05, 0.075, 0.1, 0.15, 0.2 and 0.3) were synthesized by the conventional single step of solid-state reaction technique. Pure Tl$_2$O$_3$, RuO$_2$, BaO$_2$, CaO and CuO of stoichiometric ratios 1-x: x: 2: 1: 2 were mixed using an agate mortar to make fine powder which was sieved in 85 μm sieve to obtain a homogeneous mixture. The powder was pressed in the form of a disc of dimensions 1.5 cm diameter and 0.3 cm thickness. Then the samples were wrapped in a silver foil, in order to reduce thallium evaporation during the preparation. All the operations were carried out in a glove box under argon atmosphere in order to prevent absorption of moisture and CO$_2$. Finally, the samples were heated in a sealed quartz tube to 840 °C with a heating rate of 4°C/min, and held at this temperature for three hours, then cooled to room temperature with a rate of 6 °C/min.

The synthesized samples were characterized by XRD using X’Pert’s Phillips powder diffractometer with Cu K$_\alpha$ radiation ($\lambda$=1.54056 Å). The grain size and homogeneity of the samples were identified using a Jeol scanning electron microscope JSM-5300, operated at 25 kV, with a resolution power of 4 nm.

The electrical resistivity of these samples was measured by the conventional four-probe technique in a temperature range from 300K down to 20K. The samples have the shape of parallelepipeds of approximate dimensions 15x2x3 mm$^3$, and the connections of copper leads with the samples were made using a conductive silver paint. The temperature of the samples was monitored by a Kp-Au 0.07 % Fe thermocouple and stabilized with the aid of a temperature controller to within ±0.1 K. A typical excitation of 1mA was used to avoid heating effects on the samples. The critical current density for these samples is measured at T= 68, 52 and 38 K using the conventional four-probe technique and the critical current density was calculated by the standard criterion of 1 μV.cm$^{-1}$.

### 3- Results and Discussion

The powder x-ray diffraction patterns for Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ ($x$ = 0.0, 0.025, 0.05, 0.075, 0.1, 0.15, 0.2 and 0.3) indicate that all the prepared samples are nearly single phase of Tl-1212 and are well indexed by a tetragonal unit cell of Tl-1212 with space group P4/mmm. Also, the partial replacement of Cu$^{2+}$ ions by Ru$^{4+}$ ions does not affect the tetragonal structure of Tl-1212 whereas the lattice parameters are varied. The variation of lattice parameters a and c with Ru-content for Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ is shown in figure 1. It is clear that the lattice parameter a elongates as Ru-content increases whereas the lattice parameter c contracts. This contraction can be explained according to two different reasons. The first one is attributed to the partial replacement of the Tl$^{3+}$ ions (coordination number 6: ionic radius=102 pm) by the smaller ionic radius Ru$^{4+}$ ions (6-coordinates, octahedral, ionic radius = 76 pm) which results in less spacing in the perovskite layer of Tl-1212.
structure. The second reason is that the partial replacement of Tl$^{3+}$ ions by Ru$^{4+}$ ions may lead to an increase in the oxygen-content that causes a decrease in the average oxidation state which leads to a smaller Cu-O distance within the copper-oxygen sheets (c-axis) [9]. The elongation in a as Ru-content increases is probably due to the expansion in the Cu-O bonds due to the addition of electron into antibonding orbital, resulting from the higher valence of Ruthenium. The elongation rate $\frac{da}{dx}(Ru)$ and the contraction rate $\frac{dc}{dx}(Ru)$, as estimated from figure 1, are $0.007 \ \text{Å} \ \text{at} \%$ and $0.08 \ \text{Å} \ \text{at} \%$, respectively.

![Graph showing variation of a and c with Ru-content for Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-δ}$](image)

Figure 1 variation of a and c with Ru-content for Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-δ}$.

![SEM images](image)

Figure 2a SEM for TlBa$_2$CaCu$_2$O$_{7-δ}$.

Figure 2b SEM for Tl$_{0.95}$Ru$_{0.05}$Ba$_2$CaCu$_2$O$_{7-δ}$.
The typical micrographs of Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ with $x = 0$ and 0.05, obtained from SEM investigations of the surface of the reacting pellets, are shown in figure 2a and 2b, respectively. For $x = 0$, we notice randomly oriented granular structure. Also, the grains are more connected, indicating the low porosity of the Tl-1212 sample prepared by solid-state reaction technique. It is clear that, from figure 2b, the partial replacement of Cu$^{2+}$ ions by Ru$^{4+}$ ions does not affect the granular structure of Tl-1212 but the grain-size and porosity decrease as the Ru-content increases.

Temperature dependence of electrical resistivity for Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ with $0 \leq x \leq 0.3$ is shown in figure 3. The electrical resistivity data above the superconducting transition temperature behave like normal metals for $x \leq 0.15$ and followed by superconducting transition as the temperature is lowered. With further increasing of ruthenium, upturn in electrical resistivity measurements at lower temperature is observed, indicating the localization effect or the disorder of cations and oxygen [6, 10]. The normal metallic-like behavior above $T_c$ can be interpreted by the liquid model and it reflects the spin charge separation in CuO$_2$-planes that results in the longitudinal transport relaxation rate $1/\tau \sim T$ [11]. The electrical resistivity data for $x \leq 0.15$ are well fitted, in the temperature range $130 \text{ K} \leq T \leq 290 \text{ K}$, to Matthiessen rule.

\[
\rho(T) = \rho_0 + \alpha T
\]

where $\rho(T)$ is the resistivity at temperature $T$ (in Kelvin) and $\rho_0$ is the residual resistivity. A small curvature above $T_c$ is observed for all samples, which is a characteristic of superconducting thermodynamic fluctuations. These superconducting thermodynamic fluctuations occur at finite temperatures above the superconducting transition temperature due to the appearance of Cooper pairs even above the superconducting transition temperature [12].

The superconducting transition temperature, resistivity at room temperature ($\rho_n$) and residual resistivity is plotted as a function of Ru-content in figure 4. The superconducting transition temperature is determined from the maximum point in the plotting of $(d\rho/dT)$ versus temperature. It is clear that $T_c$ enhances from 79.5 K for $x = 0$ to 104.5 K for $x = 0.05$ and then it depress to 65 K for $x = 0.3$. This behavior is explained according the hole-filling mechanism, resulting from the partial
replacement of Tl$^{3+}$ ions with higher valence Ru$^{4+}$ ions. This parabolic dependence of $T_c$ on $x$ was considered to be a typical characteristic of substituted high-temperature superconductors [13]. Our samples are prepared in air which has an oxygen pressure well above the optimum partial pressure, producing the optimum hole-concentration for maximum $T_c$. This means that the un-substituted sample has too excess of holes that depressed $T_c$, indicating that the un-substituted sample lies in the over-doped region. The addition of Ru$^{4+}$ reduces excess of holes (by hole filling mechanism) which results in the hole concentration being closer to the optimum value and $T_c$ goes up till $x = 0.05$, meaning that the optimum-doping of this phase appears at around $x = 0.05$. Further as the Ru-content increases the rate of the hole-filling increases, leading to depress $T_c$ again for $x > 0.05$, meaning that the samples in this region lie in the under-doped region. Also, the depression in $T_c$ for $x > 0.05$ could be explained according to the spin-flip process of scattering between the cooper pair and magnetic ions [14]. This process is characterized by total spin conservation in the scattering event, so the spin of the Ru atom must flip when the Cooper pairs are broken. It is convenient to discuss the results of the variation of the normal-state resistivity $\rho_n$ and the residual resistivity with $T_c$. Interesting results, for these samples, appear in the decreasing $\rho_n$ and $\rho_0$ as $T_c$ enhances and the increasing of both the normal-state resistivity and the residual resistivity as $T_c$ suppress. This suppression is considered to be related to the disorder created in the internal magnetic states of superconducting materials when they substituted with magnetic ions. The magnitude of this disorder can be characterized by the size of the magnetic moment, creating by the magnetic ions.

Figure 4 Variation of $T_c$, $\rho_n$ and $\rho_0$ with Ru-content.

Figure 5 Variation of transport current density at three different temperatures 38, 52 and 68 K in zero applied magnetic fields for Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-\delta}$ with $0 \leq x \leq 0.15$. The results show that, for all temperatures, $J_c$ increases as $x$ increases from 0 to 0.05 before decreasing with further increase in $x$. Also, $J_c$ decreases with increasing temperature, resulting from the thermally activated flux creep [15]. The enhancement of $J_c$ till $x = 0.05$ may be due to different aspects. The first one may
be due to the partial replacement of Tl$^{3+}$ ions by Ru$^{4+}$ ions enhances the amount of Tl-1212 phase. The second aspect may be due to lattice defects produced from the partial substitution of Tl$^{3+}$ by Ru$^{4+}$ ions that enhance the flux pinning. The decrease in the current density for $x > 0.15$ is attributed to the increase of the grain boundaries resistance and the reduction of the flux pinning inside the samples. Also, the formation of secondary phases plays an important role for suppressing $J_c$.

4- Conclusions

The structure, resistivity and transport current density of Tl$_{1-x}$Ru$_x$Ba$_2$CaCu$_2$O$_{7-δ}$ with $0 \leq x \leq 0.15$ have been investigated. The structure analysis implied that the lattice parameter a was elongated as Ru-content increased whereas the lattice parameter c was contracted. The superconducting transition temperature and transport current density were enhanced as Ru-content increased from 0 to 0.05 and then decreased. The enhancement of $T_c$ was discussed according to the hole-filling mechanism where as the enhancement in $J_c$ was attributed to the enhancement of both the mount of Tl-1212 phase and flux pinning. The depression in $T_c$ for $x > 0.05$ was discussed according to the hole-filling and Cooper pair breaking mechanisms, whereas the depression in $J_c$ was explained according the increasing of secondary phases and grain boundaries resistance.

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