The Role of Tl Substitution on Superconducting Properties for Hg-1223 System

M.F.A.Alias*, B. A. Aljurani, and G.Y.Hermiz
Department of Physics, College of Science, University of Baghdad,
*Corresponding author: may20131313@yahoo.com

Abstract. High temperature superconductors with a nominal composition Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ for (0≤x≤0.4) were prepared by two-step solid state reaction in air. The effect of the substitution of Tl for Hg, oxygen content (δ) and sintering time (20-200h) on the Hg-1223 superconductivity system has been investigated to obtain the optimum conditions for the formation and stabilization of the high critical temperature (Tc). The results showed that the optimum sintering temperature for the prepared samples was equal to 880 ºC, whereas the sintering time is equal to 100 h. The quantity of the element content for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ system were carried out using x-ray fluorescence (XRF). X-ray diffraction (XRD) analysis showed a tetragonal structure with a high Tc phases (1223) as a dominant phase and low Tc phase (1212) addition to exist of some impurity phases for all samples. It was found that the change of the Tl concentrations of prepared samples produced a change in the lattice parameters, density $\rho_m$ and c/a ratio. The highest Tc for HgBa$_2$Ca$_2$Cu$_3$O$_{8+δ}$ composition was 118 K. The results for the doped samples, represented highest Tc equal to 124 K for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ sample with x=0.4. The oxygen content was not systematic changed but it played a great role in the evaluation of Tc.

Keywords: Hg-1223, Tl substitution effect, Structural properties, HTSC

1. Introduction

After the discovery of high temperature superconductivity in Bi-Sr-Ca-Cu-O (BSCCO) system [1] Putilin et al.[2] in 1993 was first observed superconducting in mercury-based cuprates HgBa$_2$Ca$_{n}$Cu$_{n+2}$O$_{2n+2+δ}$ [n: the number of consecutive Cu-O layers] with the compound HgBa$_2$CuO$_{4+δ}$ (Hg-1201, Tc= 94 K). The compound extended to a homologous series of Hg-1212 (n=2), Hg-1234 (n=4) and Hg-1245 (n=5) having Tc= 120, 126 and 101 K, respectively [2, 3]. In the same year the highest critical temperature [n=3, Tc =133 K] among oxide superconductors has been reported by Schilline et al.[3]. Application of pressure at 29 GPa [4] can increase the critical temperature of the second member to 154K and that of the third to 164K at 31 GPa [4,5]. While partial substitution of Hg$^{+2}$ by ions of various radii and valance such as Tl$^{+3}$ in HgBa$_2$Ca$_2$Cu$_3$O$_{8+δ}$ compound may affect the high temperature superconductor HTSC phase formations, chemical stability and superconducting properties[6].

Die et al. [7] showed that the transition temperature Tc increased to 138 K for a nominal composition of Hg$_{0.8}$Tl$_{0.2}$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$, while Wagner et al. [8] obtained Tc around 135 K and δ = 0.18 for Hg-1223. They studied the tetragonal phase transformation by neutron powder diffraction technique founding that the lattice parameter was around a = 3.8478Å and c = 15.7782Å. Whereas Pandy et al. [9] synthesized the Tl - doped Hg - based HTSC bulk material corresponding to Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ with x = 0.2, 0.4, 0.5, 0.6 and 0.8. They found the variation of Tc from ~ 106 to ~ 133 K for under doped samples and from ~ 106 to ~ 129 K for over doped samples. Microstructure investigations revealed the presence of ordered and /or disordered stacking faults and the accompanying poly type like regions.

Giri et al. [10] studied structural / microstructures variations of the as synthesized (HgTl$_{0.2}$Bi$_{0.1}$) Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ HTSC phases with x = 0.05, 0.1, 0.15) and different nominal compositions employing transmission electron microscopic (TEM) technique. The TEM revealed the presence of defect
substructure and staking faults. The as synthesized samples exhibited stability and have T\textsubscript{c} (onset) of 133 K. They found that the phase (HgTl\textsubscript{0.1}Bi\textsubscript{0.1})-1223, had the highest density of ordered defect substructure and exhibited the highest integrain critical current density (J\textsubscript{c} = 6.2×10\textsuperscript{6} A/cm\textsuperscript{2}). Powder diffraction data for high temperature superconducting compound Hg\textsubscript{0.8}Tl\textsubscript{0.2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8+δ} at pressure range 0–20 GPa and temperature interval 100–300 K were studied by S. Titova et al. [11]. They found that Ba-atoms do not shift towards HgO\textsubscript{x}-planes and splitting of BaO-planes do not decrease with external pressure.

The effect of neutron irradiation on the microstructure properties of Hg\textsubscript{1-x-y}Tl\textsubscript{x}Pb\textsubscript{y}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8+δ} for 0≤x≤0.4 and 0≤y≤0.4 were investigated by Ghazala et al.[12]. They found that the microstructure for most samples before irradiation was to be dense and the morphology of these samples shows needle–like and plate–like layered for different compositions. While irradiation with fast and thermal neutrons induced more voids and defect in most of the samples.

In this paper, we studied the effect of Tl substitution on the superconducting properties such as electrical resistivity, transition temperature and structure of HBCCO system.

2. Experimental work

Appropriate weights of pure materials Hg\textsubscript{2}O, BaCO\textsubscript{3}, CaO, CuO, and Tl\textsubscript{2}O\textsubscript{3} in proportion of their molecular weights were used in order to prepare the samples by two step solid state reactions. During the first step, mixing the oxides, and carbonates of Ca, Cu, and Ba developed Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8} precursor. The mixture homogenization takes place by adding a sufficient quantity of 2-propanol to form a paste, during the process of grinding for about (50-60) min. Measuring the weight of the dried mixture (w\textsubscript{1}), and put it in an alumina crucible, calcined in a tube furnace in air that has programmable controller type (Eurptherm818) for 24 hours at 1073K with a rate of 275K / min. In the second step, the Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8} precursor was regrind again and mixed with Hg\textsubscript{2}O and Tl\textsubscript{2}O\textsubscript{3} to obtain the nominal compositions Hg\textsubscript{1-x}Tl\textsubscript{x}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8+δ}, where x varied from 0 to 0.4. This mixture was then pressed into pellets 1.3 cm in diameter and (0.2 – 0.3) cm thick, using hydraulic type (SPECAC), under pressure of 0.7GPa.

The pellets were pre sintered at 1153K for 100 h with a rate of 393K /h and then cooled to room temperature by the same rate of heating. The x-ray fluorescence (XRF) was used to determine the quantity of the element content for Hg\textsubscript{1-x}Tl\textsubscript{x}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8+δ} system. The structure of the prepared samples was obtained by using X-ray diffractometer (XRD) type (Philips) with the Cu\textsubscript{Kα} source. A computer program was established to calculate the lattice parameters a, b, and c. The program is based on Cohen's least square method [13].

Four probe dc method at temperature range (77-300) K was used to measure the resistivity (ρ) and to determine the critical temperature (T\textsubscript{c}). The amount of oxygen content (δ) was determined from a simple chemical experiment method called iodometric titration[14] for the samples HgBa\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{δ}, and Hg\textsubscript{1-x}Tl\textsubscript{x}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{δ} with different nominal composition. The extra oxygen content (δ) is directly associated with the average oxidation state of copper (ν\textsubscript{avCu}). Assuming ν\textsubscript{Hg} = ν\textsubscript{Ba} = ν\textsubscript{Ca} = +2, ν\textsubscript{O} = - 2, one can obtain for Hg – based superconducting cuprates the following correlation between δ and ν\textsubscript{avCu}[15,16]:

\[ \nu_{avCu} = (2 / n) \times (n + \delta) \] ………(1)

where n is the number of CuO\textsubscript{2} planes. Density (ρ\textsubscript{m}) of unit cell of the samples were calculated using the following equation [17]:

\[ \rho = \frac{W_m}{N_a V} \] …………………..(2)

where W\textsubscript{m} is the molecular weight, N\textsubscript{a} is Avogadro's number and V is the volume of the unit cell.
3. Results and Discussion

The quantity test of the element content for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ system were carried out by XRF at different nominal composition (x= 0 and 0.2) which sintered in air. These data illustrated in Figs. (1a and b) which showed that the peaks belonging to the superconducting phase consist of Hg-Ba-Ca-Cu-O, and Hg-Tl-Ba-Ca-Cu-O, respectively. This result agree with the results reported by Xu et al.[18].

![X-ray fluorescent patterns for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples with (a) x = 0 and (b) x = 0.2.](image)

**Figure 1.** X-ray fluorescent patterns for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples with (a) x = 0 and (b) x = 0.2.
A typical XRD pattern for the Tl free samples $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ prepared by solid state reaction in air method is shown in Fig. (2), indicating the dominant phase of Hg-1223 together with amount of low-phase Hg-1212 and Hg-1234 with some impurity phase like CuO at 38.8° and CaHgO$_2$ at 15.6° and 31.2°.

**Figure 2.** X-ray diffraction patterns for $\text{Hg}_1-x\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ sample for $x = 0$.

X-ray diffraction patterns for $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$, samples in Figs. (3a-c) revealed the presence of tetragonal Hg,Tl-1223 structural phase as the dominant phase. However, some peaks attributable to impurities e.g. CaHgO$_2$ and CuO and mercury phase e.g. Hg-1212,1234 (low phases) are also observed in Fig. (3c). Our results presented are in agreement with Dai et al.[7] and Pandey et al.[9] results. The lattice parameters of the (Hg$_{0.8}$Tl$_{0.2}$)-1223 were slightly less than that of the pure Hg-1223 sample. Also they revealed that samples have a multiphase with the presence of Hg,Tl-1223 as the dominant phase. The addition of thallium introduces more oxygen atoms and stronger bonding into HgO planes, raising the vibration frequency of oxygen atoms and hence stabilizing the crystal structure of the Hg-1223 phase [17,19]. The difference in lattice parameter, c/a ratio, and density of unit cell, were illustrated in Table (1) and shown in figures. (4a and b), that are obtained from XRD patterns. Table (1) showed that the Hg-1223 has tetragonal structure with the lattice parameter $a=3.851$ Å, $c=15.813$ Å of Hg-1223, which affects the volume of the unit cell and then causes an increase of the density from 6.163 to 6.210 g/cm$^3$. 
Figure 3. X-ray diffraction patterns for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+y}$ samples at (a) $x = 0.2$ (b) $x = 0.3$ (c) $x = 0.4$. 
Table 1. Lattice parameter a, c, c/a ratio, density ($\rho_m$) and volume of unit cell at different composition of Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$.

| x  | a (Å)  | c (Å)  | c/a  | $\rho_m$ (g/cm$^3$) | V (Å$^3$) |
|----|--------|--------|------|---------------------|----------|
| 0.0| 3.851  | 15.813 | 4.106| 6.163               | 234.509  |
| 0.1| -      | -      | -    | -                   | -        |
| 0.2| 3.847  | 15.765 | 4.097| 6.226               | 233.312  |
| 0.3| 3.842  | 15.786 | 4.108| 6.236               | 233.016  |
| 0.4| 3.849  | 15.801 | 4.105| 6.210               | 234.088  |

Figure 4. Variation of (a) density of unit cell, (b) c/a ratio as a function of Tl concentration for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples sintered in air.

In order to clarify the effect of sintering time on the electrical d.c. resistivity and the critical temperature, the samples of nominal composition HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$, and Hg$_{0.6}$Tl$_{0.4}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$, were sintered in air at 880°C for periods of (20-200)h, as shown in Figs. 5 a and b. It is found from these figures that prolonged sintering time up to 100 h could improve the superconductor behavior and the T$_c$ of stoichiometric composition. Also it raised T$_c$ from 100 K to 118 K for the composition x = 0 as the time increases from 80 h to 100 h, at the same sintering temperature, while T$_c$ increased to 124 K for the composition of x = 0.4. The increased values of T$_c$ could be attributed to the increase of contact areas between grains during the sintering process and in other words, decrease of the porosity. Another feature was found that when the sintering time increase above 100 h (140 h and 200 h) the critical temperature value decrease for all the prepared samples.
Figure 5. Temperature dependence of normalized resistivity for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with (a) x=0 (b) x=0.4 sintered in air at different periods of time.

It is noted from Fig. (6) and Table (2) that the Hg$_{0.6}$Tl$_{0.4}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ sample has the highest T$_c$ of 124 K. Pandey et al.[9] found that T$_c$ increased when Tl concentration increased for the as-synthesized samples. This result is in agreement with our result of the samples as shown in Fig.(7) which indicates that the variation of transition temperature with Tl content for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples (x=0.2, 0.3 and 0.4). One can observe that Tl content plays a major role on the formation of high T$_c$ phase.

Figure 6. Temperature dependence of normalized resistivity of Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ at different x value.
Figure 7. Transition temperature as a function of Tl content for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples.

Table 2. Oxygen content, the average Cu valence and transition temperature for different composition of Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$.

| $x$ | $\delta$ | $\nu_{\text{Cu}}$ | $T_c$ (K) |
|-----|---------|-----------------|----------|
| 0.0 | 0.30    | 2.20            | 118      |
| 0.1 | 0.38    | 2.25            | <77      |
| 0.2 | 0.42    | 2.28            | 121      |
| 0.3 | 0.44    | 2.29            | 122      |
| 0.4 | 0.48    | 2.32            | 124      |

The relationship between transition temperature $T_c$ and oxygen content $\delta$ for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with $0 \leq x \leq 0.4$ can be seen in Table (2). It is to be noted from this Table that $\delta=0.48$ for the sample with $x=0.4$ to have the highest $T_c$ of 124 K is with optimum carrier concentration.

In pure Hg-1223, the interstitial oxygen occupancy $\delta=0.30$ led to a mean value of copper valency +2.20 (see Table 2). Because of the +2 valency of Hg, all the oxygen sites was not filled as compared to Tl-1223 compound. The O (4) site is partially filled with interstitial oxygen. Due to this fact, there is a great flexibility in the HgO with regard to the introduction of extra oxygen atoms through oxygenation or through introduction of other suitable elements with higher number of associated oxygen atoms in place of Hg. Thus, substituting Hg$^{+2}$ by Tl$^{+3}$ will bring in greater number of associated oxygen atoms in the metal oxide HgO layer, hence disturbing the charge balance. In an analogous manner to Tl-1223 compounds, this will lead to a change in doping level of CuO$_2$ layer by creating extra holes to offset the charge misbalance in HgO layer [7].

Fig. (8) demonstrated the variation of the average Cu valance obtained by equation (1) and oxygen content as a function of Tl concentration for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples sintered at 100h. One can observe that the average Cu valance and oxygen content increase with increasing Tl content.

Figure 8. (a) Variation of average Cu valence $\nu_{\text{Cu}}$ and (b) oxygen content $\delta$ as a function of Tl content for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ samples sintered at 100h.
4. Conclusions
The conclusion from the results for preparing Hg$_{1-x}$Tlx Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ for 0≤x≤0.4 system can be summarized as follows: HgBa$_2$Ca$_2$Cu$_3$O$_{8+δ}$ and Hg$_{1-x}$Tlx Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ for 0≤x≤0.4 synthesizing with high-T$_c$ phase and the optimum sintering time was 100 h. The substitution of Tl in Hg for the compound Hg$_{1-x}$Tlx Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ with x=0.4 has maximum value of T$_c$≈124 K. X-ray diffraction analyses for all samples have shown tetragonal structure and there is a change of lattice constants with the increase in Tl concentration.

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