

The Role of Cooling Condition on the Superconducting Properties of $Tl_{2-x}Hg_xSr_2Ca_2Cu_3O_{10+\delta}$ System

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Abstract

Solid state reaction method was used to prepare high temperature superconductor with a nominal composition $Tl_{2-x}Hg_xSr_2Ca_2Cu_3O_{10+\delta}$ ($0 \leq x \leq 1$). The effect of quenching on the superconducting properties has been investigated by preparing two sets of samples at 1133 K for 3 hrs. The superconducting properties of the samples have been examined by electrical measurements. It is found that a partial substitution for Tl by Hg increases the formation of high- T_c phase and increases its T_c . X-ray diffraction (XRD) pattern analyses have shown a tetragonal structure, and there are at least two superconducting phases.

Keywords

Superconductor, Microstructure Properties, TBCCO System

1. Introduction

The most interesting crystal chemical aspect of the high temperature superconductivity (HTSc) is that for those based on Tl, there exists not only variable numbers of Cu-O layers but also variable numbers of Tl-O layers, which provide the possibility of many compounds, in what is really an infinitely adoptive series through the process of substitution and the interrelated variation of its elements. The whole series can be written as: $Tl_mBa_2Ca_{n-1}Cu_nO_{m+2n+2}$ and $Tl_mSr_2Ca_{n-1}Cu_nO_{m+2n+2}$ [1]; the subscript m defines how many rock salt layers are present. The number of copper layers is remarkably variable, with $n = 1, 2, 3$ and 4 presently claimed to be prepared as bulk material. Even more remarkably, all compounds, synthesized in this series, are claimed to be superconducting with T_c 's greater than 80 K. The desirable phase is the $m = 2$ and $n = 3$ phase,

$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (2223) because of its higher T_c [2]. Discoveries of Tl-based system have not only set new T_c records with zero resistance up to 125 K, but also have provided a new insight into the mechanism of high- T_c oxide superconductivity [3].

Two superconducting phases, $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10+\delta}$ and $\text{Tl}_2\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_{8+\delta}$ were identified in their samples by Hazan *et al.* [4]. They found that these phases have a pseudo tetragonal unit cell ($5.40 \times 5.40 \times 36.25$) Å, corresponding to a, b and c lattice dimensions, respectively. In the same year, Parkin *et al.* [5] found that T_c in $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ system prepared by a solid state reaction method varies from 118 K to 125 K depending on preparation conditions. The transmission electron spectroscopy shows that the unit cell is a body-centered tetragonal and contains trilayer Cu perovskite units separated by bilayer Tl-O units with $a = 3.82$ and $c = 12.00$ Å. T_c (zero) was found to be 78, 96, 106, 98, 45 and 25 K for $\text{Tl}_{0.5}\text{Ca}_{1-x}\text{Pr}_x\text{Sr}_2\text{Cu}_2$ oxide sample with $x = 0, 0.1, 0.2, 0.5$ and 0.7 , respectively and for $x = 1$, the sample exhibited a semiconductor behavior.

Kaell *et al.* (1991) [6] studied the variation of T_c due to partial Sr substitution, for Ba in $\text{Tl}_2\text{Ba}_{2-x}\text{Sr}_x\text{Ca}_1\text{Cu}_2\text{O}_8$ (Tl-2212), ($x = 0 - 0.6$), and $\text{Tl}_2\text{Ba}_{2-x}\text{Sr}_x\text{Cu}_1\text{O}_6$ (Tl-2201) ($x = 0 - 0.6$). They showed that, T_c decreases rapidly with increasing Sr content for both Tl-2212 and Tl-2201 systems.

Bulk polycrystalline $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$ system has been fabricated by Ossandon *et al.* (2001) [7]. Results showed that the crystalline unit cell is tetragonal with lattice constant $a = 3.8550$ Å and $c = 29.318$ Å (cell volume of 2.18×10^{-23} m³) containing two sets of adjacent oxygen copper layers. The samples were irradiated at room temperature in air with 0.8 GeV protons. The superconductive properties of the virgin and irradiated materials were investigated magnetically.

Eu-substituted ($\text{Tl}_{0.6}\text{Pb}_{0.4}$) ($\text{Sr}_{0.9}\text{Ba}_{0.1}$)₂ ($\text{Ca}_{1-x}\text{Eu}_x$) Cu_2O_4 , for $x = 0.2, 0.4$, and 0.6 compounds were prepared by Kuzman *et al.* (2004) [8]. They demonstrated that Eu can be substituted for Ca in separating the layer between Cu-O conducting layers, Cu atoms are in the center of the basal plane of pyramids of the conducting layers, in the spacing layer Ba atoms are shown, and oxygen atoms are situated both in the corners of the pyramids and in the insulating layer, surrounded by Tl atoms.

Maysoon *et al.* [9] studied the effect of sintering time on superconducting properties of $\text{Tl}_{1.6}\text{Hg}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ and $\text{Tl}_{1.8}\text{Bi}_{0.2}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ compounds. They found that the optimum sintering time which was characteristic for the growth of high- T_c phase equal to 3 h and prolonging the sintering time to 6 h lead to decrease the transition temperature.

In this paper the impact of quenching in air was investigated on the structural and electrical properties of $\text{Tl}_{2-x}\text{Hg}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ system type 2223.

2. Experimental

The solid state reaction technique has been used to prepare homogeneous and well-defined single phase superconducting samples with uniform oxygen stoichiometry evolution of accurate physical parameters. Solid state reaction is the

least expensive and largest batch size of any powder fabrication process, the procedure involves a simple blending of the required precursors, followed by one or more reactions at a high temperature [10].

So appropriate amounts of high purity Tl_2O_3 , Hg_2O , $\text{Sr}(\text{NO}_3)_2$, CaO and CuO powders have been weighed stoichiometrically. Precursor $\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ was first prepared using high purity powders of $\text{Sr}(\text{NO}_3)_2$, CaO and CuO as starting materials. Then, Tl_2O_3 and Hg_2O were added to the mixture and grinding them in agate mortar to obtain a very fine powder. The mixtures were pressed into a pellet of (0.2 - 0.3) cm thickness and 1.3 cm diameter, under a pressure of about 3 ton/cm². The samples were sintered in air atmosphere at temperature 1133 K for 3 hrs in order to make the particles of the materials joined together and gradually reduce the volume of pore spaces between them. The most common method of determining T_c of a superconductor is the resistivity measurement by using the four-point probe method in a cryostat with presence of liquid nitrogen. The cryostat system joined to a rotary pump to get a pressure of ($\sim 10^{-2}$ mbar) inside the cryostat by using (Edward Prini 12) gage, and joined also to a sensor of a digital thermometer type (RTD), and thermocouple type (T) near the sample position. Four wires have been connected to the cryostat, the outer connection were used for supplying the sample with current from D.C power supply type (6236A triple output), while the inner connections were used to measure the voltage drop by a digital nanovoltmeter type (KETHLEY 180) with sensitivity of about (± 0.1 nanovolt).

The structure of the prepared samples was obtained by using X-ray diffractometer (XRD) type Philips having the following features (source: $\text{Cu}_{\text{K}\alpha}$, voltage: 40 kV, current: 20 mA, wavelength: 1.5405 Å). A computer program [11] was used to calculate the lattice parameters a, b and c. This program is based on Cohen's least square method [12]. Scanning electron microscope (SEM) type, Jeol model JSM-5600 has been used to study the nature of grains and to analyze the surface morphology of the samples. The oxygen content in the oxide ceramic samples was determined by the simple iodometric titration technique [13].

3. Results and Discussion

Two sets of samples were produced for each superconducting compound, the first set of samples was allowed to cool to room temperature in a tube furnace that has programmable controller with a cooling rate 275 K/min, while the second set of samples was removed from the furnace and quenched in air. **Figure 1** and **Figure 2** illustrate the variation of resistivity with temperature for $\text{Tl}_{2-x}\text{Hg}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples. It is found that the substitution of 0.1, 0.2, 0.3 and 0.4 Hg content to the composition raise the transition temperature T_c and more addition ($x = 0.5$) decrease the critical temperature, and when $x \geq 0.6$ our apparatus could not help us to obtain the value of $T_{c(\text{off})}$ because it is less than the liquid nitrogen temperature. This result indicates that the Hg has catalytic effect on the reaction to form the high- T_c phase (HTP) within the range $x = 0.1 - 0.4$.

However, certain amount of Hg is necessary for the occurrence of this reaction, while excessive Hg substitution promotes another reaction, which is likely to assist the formation of low- T_c phase instead of the high- T_c phase [14] [15] [16].

From these figures and **Table 1** the role of quenching enhancement on the critical transition temperature has been seen.

The above results demonstrate that it is interesting to prepare variety of Tl-2223 samples in order to obtain the optimum high- T_c phase. Similar explanation was reported by Hermiz *et al.* [17]. Thus, such comprehensive and complementary procedures should be used for investigating TlSrCaCuO system to explore if there will be a light at the end of the channel to arrive to or near room temperature; high temperature is required for the initiation of the formation reaction of superconducting compound; a short duration heating minimizes the decomposition and quenching stabilizes the superconducting phase.

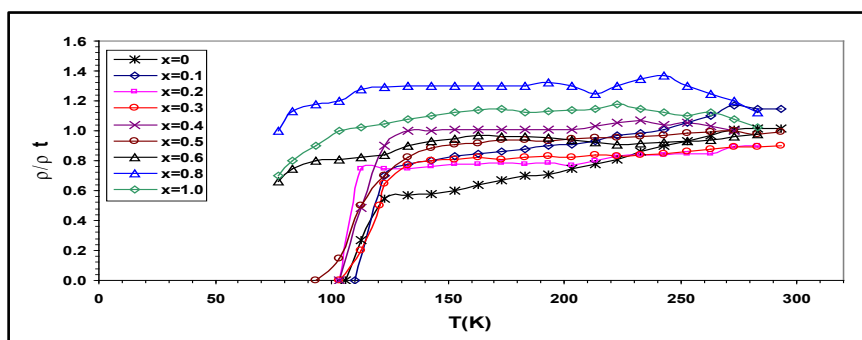


Figure 1. Temperature dependence of normalized resistivity for $Tl_{2-x}Hg_xSr_2Ca_2Cu_3O_{10+\delta}$ samples for different Hg content (samples furnace cooled).

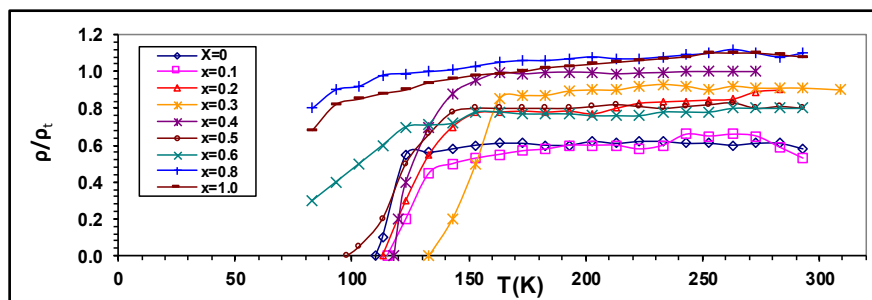


Figure 2. Temperature dependence of normalized resistivity for $Tl_{2-x}Hg_xSr_2Ca_2Cu_3O_{10+\delta}$ system with different Hg content (samples quenched in air).

Table 1. Variation in T_c values, lattice parameters and oxygen content with different cooling condition.

Sample	Cooling condition	a (Å)	c (Å)	T_c (K)	δ
$Tl_2Sr_2Ca_2Cu_3O_{10+\delta}$	Furnace cooled	4.350	33.78	110	0.189
	Quenched in air	4.150	34.37	118	0.250
$Tl_{1.6}Hg_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$	Furnace cooled	3.721	37.616	120	0.298
	Quenched in air	4.056	37.889	130	0.301

Some representative XRD patterns of the samples furnace cooled and quenched in air are shown in **Figures 3-6**. It is seen from these figures that the quenching enhances crystallinity and, the main peaks of these samples are attributed to the Tl-2223 phase with intensity higher than the furnace cooled samples peaks. The values of the lattice parameter a and c for these samples are listed in **Table 1**. This table shows an increase of the c -axis lattice constant for Hg-doped samples as compared with the undoped samples, the reason is due to the substitution of Hg for Tl where the ionic radii of Hg^{2+} (1.11 Å) is longer than that of Tl^{3+} (0.95 Å) as mentioned previously which renders c -parameter to be longer or get deformed [18].

Most of the physical properties are very sensitive to the oxygen content in high- T_c superconductors. Therefore, it is important to report the oxygen content of the sample on which the physical measurements are made.

The variation of cooling condition reflected on the T_c and δ values, whereas higher T_c and δ values are recorded in the quenched in air samples rather than the furnace cooled samples. This indicates that the increase in the T_c and δ values are attributed to the increase of oxygen absorption during crystallization process of the superconductors [19].

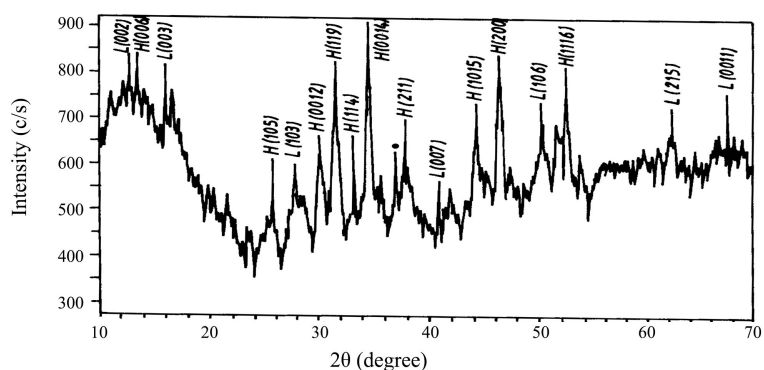


Figure 3. X-ray diffraction patterns of $\text{Tl}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples sintered at 1133 K for 3 hrs in air (samples furnace cooled). H—High T_c phase, L—low T_c phase, —impurity phase ($\text{Sr}_2\text{Ca}_2\text{Cu}_7\text{O}$).

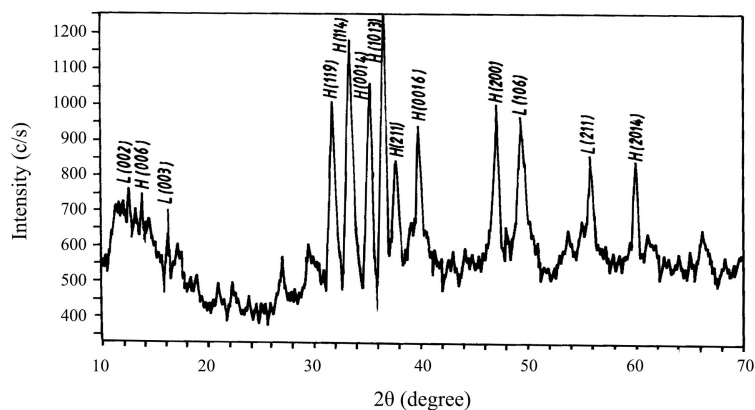


Figure 4. X-ray diffraction patterns of $\text{Tl}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples sintered at 1133 K for 3 hrs (samples quenched in air). H—High T_c phase, L—Low T_c phase.

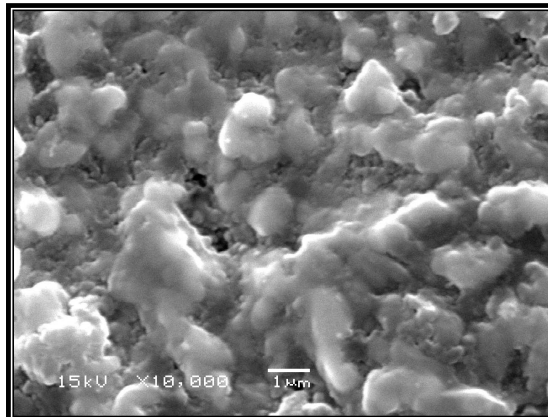


Figure 8. SEM micrographs of the fracture surfaces of $\text{Tl}_{1.6}\text{Hg}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ quenched sample.

4. Conclusion

A partial substitution of Tl by Hg was found to promote the formation and grain growth of Tl-2223 phase and then enhance the T_c value. XRD pattern analyses have shown a tetragonal structure, and there were at least two superconducting phases. The dominant phase showed the mean composition corresponding to Tl-2223. Samples quenched in air showed a higher T_c value, less porous, higher growth and bigger grains than the furnace cooled sample.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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