Superconductivity Measurements of (Hg,Tl)1223 Compound Prepared in Capsule

B. A. Aljurani*, G.Y. Hermiz and M.F. Alias
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Received: 4/8/2020 Accepted: 27/2/2021

Abstract
In this paper, investigations were carried out on the effects of simultaneous partial substitution of Tl at the Hg site on the physical properties of an Hg1-xTlxBa2Ca2Cu3O8+δ cuprate superconductor with x = 0, 0.1, 0.2, 0.3 and 0.4. Two steps of the solid state reaction method were used to prepare samples in capsule. The results showed that the optimum sintering temperature was equal to 850 °C and the sintering time was equal to 20 h for the prepared samples. The best conditions for constitution and stabilization of the high Tc phase-1223 were obtained by investigating the effects of Tl substitution on Hg site and oxygen content (δ) on the superconducting properties. Structural investigation revealed that all the samples have a tetragonal structure with two phases, namely an Hg-1223 high Tc phase as a main phase and an Hg-1212 low Tc phase. Besides, some impurity phases like CuO and CaHgO2 were found. The increase of Tl content in Hg1-xTlxBa2Ca2Cu3O8+δ compound from 0 to 0.4 caused a change in the lattice parameter, density of the unit cell (p_m), and c/a values. HgBa2Ca2Cu3O8+δ compound exhibited a critical transition temperature that is equal to 115 K. On the other side, the results showed that the highest Tc was 119 K for Hg0.8Tl0.2Ba2Ca2Cu3O8+δ. The oxygen content (δ= 0.46) was expected to be the optimum hole doping for Hg0.8Tl0.2Ba2Ca2Cu3O8+δ compound, which means in our opinion that δ plays a remarkable role in the assessment of Tc.

Keywords: Hg-1223 in capsule, Substitution influence, High temperature superconductor

القياسات الفائقة التوصيل للمركب (Hg,Tl)1223 المحضر في الكبسولة

بشيراء عبد الوهاب الجوراني، غزاله يلدا هرمز، ميسون فيصل احمد الياس
قسم الفيزياء، كلية العلوم، جامعة بغداد

الخلاصة
في هذا البحث تم استقراء تأثير التعويض الجزئي المتزايد للثالوث Tl في مواقع الزئبق على الخواص الفيزيائية للمركب الفائق التوصيل Hg1-xTlxBa2Ca2Cu3O8+δ وقيم 4 Hg1-xTlxBa2Ca2Cu3O8+δ لمثاليهم x=0,0.1,0.2,0.3,0.4. حضرت النماذج في الكبسولة وتم تجربة تقنية تفاعل الحالة الصلبة. وثبت النتائج أن درجة حرارة التبريد المثلى هي 980 °C وتم تبخير مصبير إلى 180 لجميع النماذج المصضة بهذه الطريقة. إن أفضل شروط تكون واستقرار التوزع ذي درجة الحرارة العالي 1223 تم الحصول عليه من خلال استقراء تأثير تعويض الثالوث بالواقع الزئبق Hg ومحتوى الأوكسجين δ على الخواص الفائقة التوصيل.

*Email: b_a_jurani@yahoo.com

ISSN: 0067-2904

DOI: 10.24996/ijs.2021.62.9.9
1. Introduction

Mercury-based cuprates HgBa$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$, where n indicates the set of successive Cu-O layers, was first discovered in 1993 [1]. Types of superconductors as Hg-based high Tc are interesting for researchers because they have higher superconducting transition temperature (Tc =133 K for HgBa$_2$Ca$_2$Cu$_3$O$_y$) [2]. For these compounds, the absence of trivalent element is a reason for the presence of excess oxygen voids, which probably render the Hg– based cuprates unstable, consequently the hard in its synthesis as in matching with other family of cuprate oxide [3-5]. Many efforts to overcome these problems have been exerted. Partial substitution of Hg$^{2+}$ using different radii and valences of ions, such as Tl$^{+}$ in the HgBa$_2$Ca$_2$Cu$_3$O$_{y+\delta}$ system, perhaps affect the figuration, structural stabilization and superconducting characteristics of phases [6, 7].

Hür et al. [8] prepared the mercury base superconductor (Hg, Tl)-1212,Hg$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_4$Sr$_2$Cu$_{10}$O$_{28}$ at (x=0.14) by using the solid state reaction method. The examination of X-ray powder diffraction revealed a tetragonal symmetry of the crystal with a space group of Pn/m. They found that the value of Tc was 128 K, which is a Tc value for a synthesized sample sintered at 400 °C for 6 h. The sample was annealed in an argon atmosphere and the Tc was increased to 132 K. In addition, they found that Tl substitution at the Hg site is an evidence of stabilization of the (Hg, Tl) – 1223 phase and the value of critical current density is approximately doubled in comparison to that value for the pristine Hg Ba$_2$ (Ca$_{1+\delta}$Sr$_2$)$_2$Cu$_{1+\delta}$O$_{y+\delta}$. The influence of preparation method and n values on the critical temperature of Hg$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n+2+\delta}$ for n=1-5 system was studied by Hermiz et al. [9] using solid state reaction process with two steps. The value of Tc was enhanced by increasing n value up to 3. However, a reduction of Tc was found at higher values of n. Their results indicated that the maximum value of Tc for the prepared samples of (Hg-Tl)-1223 was 125 K.

Alas et al.[10] prepared superconductors at high temperature with Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{y+\delta}$ as a nominal composition for (0≤x≤0.4) via a two- steps solid state reaction in air. Their results showed that the optimum sintering temperature was 880 °C, whereas the sintering period was 100 h. The TI substitution in Hg sites for Hg$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_2$Cu$_3$O$_{y+\delta}$ compound has maximized the value of Tc to ≈ 124 K. For all samples, using X-ray diffraction analyses, a tetragonal structure was noted, in addition to the change in the lattice parameters with the Ti content increment.

In previous works [11,12], we studied the effect of neutrons (thermal and fast) irradiation for different times on the structure , transition temperature (Tc) and superconducting phase morphology of Hg$_{1-x}$Tl$_x$Pb$_2$Ba$_2$Ca$_2$Cu$_3$O$_{y+\delta}$ for (0≤x≤0.4) and (0≤y≤0.4) compositions using scanning electron microscopy. We found that the elongated grains are accountable for the superconductivity, which could occur for high and low Tc phases. The defects, such as amorphous phase and grain boundary, that influence critical current density were observed. We concluded that the transition temperature is reasonably dependent on microstructural features and the microstructural details may influence transport Jc.

This paper studies the effects of simultaneous partial substitution TI at the Hg site on the physical properties, such as the structure, critical temperature and electrical resistivity, of Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{y+\delta}$ compound with x= 0, 0.1, 0.2, 0.3 and 0.4, which is prepared in capsule.

2. Experiments

By choosing suitable weights of HgO, BaCO$_3$, CaO, CuO, and Tl$_2$O, proportional to their molecular weights, samples were prepared by two steps of the solid state reaction method. The first step involved mixing the oxides and carbonates of Ca, Cu, and Ba to prepare Ba$_2$Ca$_2$Cu$_3$O$_y$ precursor.
The blend homogenization was carried out by admixing a suitable quantity of isopropanol to make dough, through the operation of grinding which took about sixty minute. The dried mixture was weighted and placed in an alumina crucible, then calcined in air using a tube furnace that run by programmable controller (Eurptherm818) for 24 hours at 800 °C with a rate of 2°C / min. The second step involved a reground process again and mixing with Hg₂O and Tl₂O₃ to obtain a nominal compound of Hg₁₋ₓTlₓBa₂Ca₂Cu₃O₈₊δ. Next, the mixture was subjected to pressing into pellets with 1.3 cm diameter and 0.2 – 0.3 cm thickness, using a hydraulic device (SPECAC), under 0.7GPa pressure.

The samples were set in a sealed quartz tube evacuated by a rotary pump to obtain a pressure of 10⁻² mbar. Then these samples were placed in a programmable furnace to raise the temperature up to 600 °C for one hour with a rate of 200 °C/h, thereafter reaching 860°C at a rate of 100 °C/h and kept at this temperature for 20h. In the end, and by the same rate of heating, the furnace was cooled to room temperature.

In order to determine the electrical resistivity (ρ) and critical temperature (Tₘ), the linear four point probe dc technique at a temperature range of (77-300) K was used.

X-ray diffractometer (XRD) (Philips) with the CuKα source was used to identify the structure of the prepared samples. A computer code was accomplished to calculate the lattice constants a, b, and c. The code was built based on Cohen's least square method [13].

The parameters of the extra oxygen content (δ), mean oxidation state of copper (νavCu) and the density of the unit cell (ρm) for the specimens were estimated as was explained in previous papers [10, 14].

![Figure 1](image.png)

**Figure 1**-patterns of x-ray for fluorescent HgBa₂Ca₂Cu₃O₈₊δ sintered in capsule.

3. Results and Discussion

The test of elements’ quantities for the HgBa₂Ca₂Cu₃O₈₊δ compound sintered in capsule was carried out by XRF. Data illustrated in Figure-1 show that the grains belonging to the superconducting phase consist of Hg-Ba-Ca-Cu-O. This result is in agreement with that reported by Xu et al.[15]. They found that the capsulation method stops the runaway of Hg element from the mixture.

Figure-2 represents an XRD pattern of the Tl free specimen HgBa₂Ca₂Cu₃O₈₊δ, which indicates the Hg-1223 high Tc phase, as a main phase, and Hg-1212 with Hg-1234 as low Tc phases, accompanied by some impurity phases like CuO and CaHgO₂. The appearance of more than two phases could be related to the stacking faults along the c-axis [16]. It should be mentioned that the intensities of the diffraction peaks have a relatively slight variation for different samples.
Aljurani et al.  
Iraqi Journal of Science, 2021, Vol. 62, No. 9, pp: 2934-2939

Figure 2-pattrens of x-ray diffraction for (a) HgBa2Ca2Cu3O8+δ and (b) Hg0.8Tl0.2Ba2Ca2Cu3O8+δ sintered in capsule.

Table 1-Lattice constants, c/a and density ρm, for different composition of Hg1-xTlxBa2Ca2Cu3O8+δ.

| x  | a(Å)  | c(Å)  | c/a   | ρm (g/cm³) |
|----|-------|-------|-------|------------|
| 0  | 3.848 | 15.781| 4.101 | 6.210      |
| 0.1| -     | -     |       |            |
| 0.2| 3.868 | 15.915| 4.115 | 6.391      |
| 0.3| -     | -     |       |            |
| 0.4| -     | -     |       |            |

From Table (1), the tetragonal structure is clear in both Hg-1223 and (Hg,Tl)-1223 samples, which have lattice constant values of a=3.848 Å and c=15.781 Å for the thallium free sample and a=3.868 Å and c=15.915 Å for x=0.2. This impacts the unit cell volume and in consequence causes an enhancement of the unit cell density from 6.210 to 6.391 g/cm³.

The step of adding thallium yields additional oxygen atoms which might bond into HgO planes, turning up the oscillation frequency of excessive oxygen content and, subsequently, stabilizing the construction building of the Hg-1223 phase [17]. The obtained lattice constants, c/a, and density of unit cell and their differences based on XRD patterns are shown in Table-1.

It is noticed from Figure-3 and Table-2 that the HgBa2Ca2Cu3O8+δ sample has 115 K as Tc value , while 119 K is the highest Tc value of Hg0.8Tl0.2Ba2Ca2Cu3O8+δ. The addition of small amounts of Tl enhances the solid state reaction rate and greatly increases the superconducting volume fraction, then increases the transition temperature [14]. Besides, 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 [15].

Our observations of the encapsulation method are similar to those of Dai et al.[18]. They found that the superconducting transition temperature of the Tl- substituted on the Hg-1223 was enhanced, and that Hg0.8Tl0.2Ba2Ca2Cu3O8+δ Sample had a value of 133 K which increased to 138 K after annealing in oxygen.

Furthermore, Pandey et al.[17] found that Tc went up when increasing Tl content in the as-synthesized specimen .Their results coincides with the obtained result here based on the specimens with x=0.2, which indicates that Tl has the most important part and has influences on the configuration of high Tc phases.

The extra oxygen content (δ) was found by using a simple chemical experimental procedure named “Iodometric Titration” [19] for Hg1-xTlxBa2Ca2Cu3O8+δ samples with x=0 and 0.2. The connection between oxygen content δ and transition temperature Tc for Hg1-xTlxBa2Ca2Cu3O8+δ with (0-0.4) can be noticed in Table-2.
Figure 3- Normalized resistivity and temperature relation for Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+δ}

Table 2- Excessive of oxygen atoms, mean Cu valence and critical temperature values for Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+δ}.

| x   | δ   | v_{Cu} | T_c (K) |
|-----|-----|--------|---------|
| 0   | 0.32| 2.21   | 115     |
| 0.1 | -   | -      | semi    |
| 0.2 | 0.46| 2.30   | 119     |
| 0.3 | -   | -      | <77     |
| 0.4 | -   | -      | <77     |

It is observed from this Table that the δ=0.46 value for Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+δ} has a critical temperature of 119 K, which represents the highest value with ideal carrier concentration. For pure Hg-1223, the occupancy of interstitial oxygen δ= 0.32 leads to an average value for copper valency +2.1. On account of the valency +2 of Hg, all the oxygen positions are empty as compared to (Hg,Tl)-1223 compound. The O (4) position is partly occupied by oxygen atoms. In relation to this fact, there is a large elasticity in HgO which is related to the injunction of extra oxygen atoms during oxygenation or through immersing of other suitable elements with a large amount of related oxygen atoms in place of Hg. Thus, replacing mercury ions by thallium ions yields a higher amount of related oxygen atoms (from 0.32 for pure sample to 0.46 when x became 0.2) in the metal oxide HgO layer, consequently disarranging the charge equilibrium. In comparison with Tl-1223 system, this will drive a modification in the doping plane of CuO_2 by making more voids to compensate the imbalance of the charge in HgO layer [20].

4. Conclusions

In this article, it was found that the optimum sintering temperature for samples prepared in capsule for 20 h was 850 °C. The maximum transition temperature was equal to 119K for Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+δ} compound. The encapsulation method has proved to be the best method for achieving a strong and high density structure with short sintering time and less run away of Hg, as shown in x-ray fluorescent results. However, this method is difficult in fabrication with high cost if compared with synthesis in air.

References
1. Putlin, S.N.; Antipov, E.V.; Chmaissem, O.; and Marezio, M. 1993. Superconductivity at 94 K in HgBa_2CuO_{4+δ}. Nature, 362: 226-228.
2. Schilling, A.; Cantoni, M.; Gou, J.D. and Ott, H.R. 1993. Superconductivity above 130 K in the Hg-Ba-Ca-Cu-O system, Nature, 363: 56-58.
3. Yamawaki, K.; Sasaki, S.; Tanaka, M.; Yamauchi, H. and Lee, S. 2001. Cation distribution in Hg sites of (Hg,Pb)-1223 determined by synchrotron X-ray anomalous scattering” Physica C, 361: 22-30.
4. Pavirov, D.A. 2004. *Synthesis and Properties of Substituted Hg-Based Superconductors* “Ph.D. Thesis, Department of Inorganic Chemistry, Stockholm University.

5. Atikur Rahman, Md; Zahidur Rahman, Md.; Nurush Samsuddoha,Md. 2015. A Review on Cuprate Based Superconducting Materials Including Characteristics and Applications. *American Journal of Physics and Applications*, 3(2): 39-56.

6. Liu, J.Z.; Chang, I.C.; Lan, M.D.; Klavins, P. and Shelton,R.N.1995. Superconductivity above 130K in Tl$_1$$_n$Tl$_1$$_1$Ba$_2$Ca$_2$Cu$_y$O$_{8+delta}$. *Physica. Superconductivity*, 246(3-4): 203-206.

7. Abbas L.K. 2005. Effect of Ag and In Substitution on $T_c$ and Superconducting Properties of the Hg$_{1-x}$(Ag, In)$_x$Ba$_2$Sr$_2$Ca$_3$Cu$_4$O$_{8+delta}$. Ph.D. Thesis, Department of Physics, College of Science, Baghdad University, Iraq.

8. Hur,N.H.NKim,N.H.Lee,K.W.Park,Y.K.andPark,J.C. 1994. Synthesis and characterization of a new mercury-based superconductor, Hg$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_{1-x}$Sr$_x$Cu$_2$O$_{6+delta}$, *Physica C*, 231(1–2): 4-8.

9. Hermiz, G.Y. and AL-Beyaty,E.Kh.2011. Electrical properties of Hg$_{0.5}$Tl$_{0.5}$Ba$_2$Ca$_{1-x}$Sr$_x$Cu$_2$O$_{6+delta}$ for (n=1-5) HTSC system *Ceramic Transactions*, 226: 129-136.

10. Aliak, M.F.A .Aljurani, B.A. and Hermiz,G.Y. 2020 The Role of Tl Substitution on Superconducting Properties for Hg-1223 System,1st International Conference in Physical Science and Advance Materials IOP Conf. Series: *Materials Science and Engineering*, 757: 012058.

11. Aljurani, B.A.; Hermiz, G.Y. and Aliak, M.F.A. 2009.Effect of Neutrons on the superconducting properties of Hg$_{1-x}$TlxPb$_2$Ba$_2$Ca$_2$Cu$_y$O$_{8+delta}$ for (0≤x≤0.4) and (0≤y≤0.4) System. *Iraqi j. Science*, 50: 1636-1645.

12. Hermiz,G.Y. Aliak, M.F.A. and Aljurani,B.A. 2017. Effect of Neutrons Irradiation on the Microstructure Properties of Hg$_{1-x}$TlxPb$_2$Ba$_2$Ca$_2$Cu$_y$O$_{8+delta}$ for (0≤x≤0.4) and (0≤y≤0.4) System. *Indian Journal of Natural Sciences*, 8(43): 12642-12650.

13. Ferguson, I.F. Rogerson,A.H. 1984. A program for the derivation of crystal unit cell parameters from x-ray powder diffraction measurements *Computer Phys. Communication*, 32: 95.

14. Aljurani, B. A. 2007. *Characterization and properties of the superconducting Hg$_{1-x}$yTlxPb$_2$Ba$_2$Ca$_2$Cu$_y$O$_{8+delta}$ system*. Ph.D. Thesis, Department of Physics, College of Science, Baghdad University, Iraq.

15. Xu, Q.L.; Foong, F. Liou, S.H. Cao, L.Z. and Zhang,Y.H.1997. Synthesis and thermal stabilization of nearly single-phase superconductor HgBa$_2$Ca$_2$Cu$_3$O$_{8+delta}$ by Tl substitution *Supercon.Sci. Technol.*, 10: 218.

16. Makadzi, M.N. Hermiz, G.Y. AL-Ani, S.K. and AL-Shakarchi,E.KH. 2007. Optimization of structure and preparing conditions of HTSC (Bi$_{0.8}$Pb$_{0.2}$)$_2$(Sr$_{1-x}$Ba$_x$)$_2$Ca$_2$Cu$_2$O$_{10+delta}$ to obtain the Highest $T_c$. *Iraqi j.of Science*, 48(1): 89-96.

17. Pandey, A. K.Verma, D.V. and Srivastava,O.N. 1998. Investigations on the Tl-doped Hg–Ba–Ca–Cu–O high temperature superconductors in regard to hole doping and microstructural characteristics, *Physica C*, 306: 47-57.

18. Dai, F. Chakoumakos, B.C. Sun, G.F. Wong, K.W. Xin, Y. Lu, D.F. 1995. Synthesis and neutron powder diffraction study of the superconductor HgBa$_2$Ca$_2$Cu$_3$O$_{8+delta}$ by Tl Substitution *Physica C*, 243: 201-206.

19. Manthiram, A. Swinnea, J.S. Sui, Z.T. Steinfink, H. and Goodenough, J.B.1987. The influence of oxygen variation on the crystal structure and phase composition of the superconductor yttrium barium copper oxide (YBa$_2$Cu$_3$O$_{7+delta}$) *J. Am. Chem. Soc.*, 109(22): 6667-6669.

20. Wagner, J.L. Hunter, B.A. Hinks, D.G. Jorgensen, J.D.1995. Structure and superconductivity of HgBa$_2$Ca$_2$Cu$_3$O$_{8+delta}$. *Phys.Rev.B*, 51(21): 15407-15414.