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

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 $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$ 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 T_c 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 T_c phase as a main phase and an Hg-1212 low T_c phase. Besides, some impurity phases like CuO and $CaHgO_2$ were found. The increase of Tl content in $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$ compound from 0 to 0.4 caused a change in the lattice parameter, density of the unit cell (ρ_m), and c/a values.

$HgBa_2Ca_2Cu_3O_{8+\delta}$ compound exhibited a critical transition temperature that is equal to 115 K. On the other side, the results showed that the highest T_c was 119 K for $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$. The oxygen content ($\delta$= 0.46) was expected to be the optimum hole doping for $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ compound, which means in our opinion that δ plays a remarkable role in the assessment of T_c.

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

<div dir="rtl">

القياسات الفائقة التوصيل للمركب (Hg,Tl)ـ1223 المحضر في الكبسولة

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

الخلاصة

في هذا البحث تم استقصاء تأثير التعويض الجزئي المتزامن للثاليوم Tl في مواقع الزئبق Hgعلى الخواص الفيزيائية للمركب الفائق التوصيل$Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$ ولقيم x=0,0.1,0.2,0.3,0.4 حضرت النماذج في الكبسولة وبمرحلتين وباستخدام تقنية تفاعل الحالة الصلبة.بينت النتائج ان درجة حرارة التلبيد المثلى هي C° 850 وزمن تلبيد مساوي الى 20h لجميع النماذج المحضرة بهذه الطريقة.

ان افضل شروط تكوين واستقرار الطور ذي درجة الحرارة الحرجة العالي 1223 تم الحصول عليه من خلال استقصاء تأثير تعويض الثاليوم Tlبموقع الزئبق Hgومحتوى الاوكسجين δ على الخواص الفائقة التوصيل.

</div>

---

*Email: b_a_jurani@yahoo.com

اوضح التحليل التركيبي ان جميع العينات المحضرة هي ذات تركيب رباعي الزوايا مع وجود طورين الطور

الفائق التوصيل العالي Hg–1223كطور متغلب مع وجود الطور الفائق التوصيل الواطئ Hg–1212مع

نسب قليلة من طور الشوائب مثل CuO وCaHgO$_2$. ان زيادة محتوى الثاليوم Tlفي المركب Hg$_{1-}$

$_x$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ x من 0 الى 0.4 ادى الى تغيير معلمات الشبيكة ,كثافة وحدة الشبيكة و c\a.

ان المركب HgBa$_2$Ca$_2$Cu$_3$O$_{8+δ}$ له درجة حرارة حرجة مساوية الى 115 كلفن .من ناحية اخرى اوضحت

النتائج ان اعلى درجة حرارة حرجة كانت 119 كلفن للمركب Hg$_{1-x}$Tl$_x$Ba$_2$Ca $_2$Cu$_3$O$_{8+δ}$.ان محتوى

الاوكسجين δ=0.46 يعتبر القيمة المثلى لتطعيم الفجوات للمركب Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ وبذا يلعب

دورا مهما في تقييم درجة الحرارة الحرجة T$_c$.

1. Introduction

Mercury-based cuprates $HgBa_2Ca_{n-1}Cu_nO_{2n+2+δ}$, where n indicates the set of successive Cu-O layers, was first discovered in 1993 [1]. Types of superconductors as Hg-based high T_c are interesting for researchers because they have higher superconducting transition temperature (T_c =133 K for $HgBa_2Ca_2Cu_3O_{8+δ}$) [2]. For these compounds, the absence of trivalent element is a reason for the presence of excessive oxygen voids, which probably render the Hg– based cuprates unstable, consequently the hard in its synthesize 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 valances of ions, such as Tl^{+3} in the $HgBa_2Ca_2Cu_3O_{8+δ}$ system, perhaps affect the figuration, structural stabilization and superconducting characteristics of phases [6, 7].

Hur *et al*. [8] prepared the mercury base superconductor (Hg,Tl)-1212,$Hg_{0.5}Tl_{0.5}Ba_2Ca_{1-x}Sr_xCu_2O_{8+δ}$ 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 P_4 / mmm. They found that the value of T_c was 128 K, which is a T_c value for a synthesized sample sintered at 400 °C for 6 h. The sample was annealed in an argon atmosphere and the T_c 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$_{1-x}$Sr$_x$)$_2$Cu$_3$O$_{8+δ}$. The influence of preparation method and n values on the critical temperature of $Hg_{0.8}Tl_{0.2}Ba_2Ca_{n-1}Cu_nO_{2n+2+δ}$ for n=1-5 system was studied by Hermiz *et al*. [9] using solid state reaction process with two steps. The value of T_c was enhanced by increasing n value up to 3. However, a reduction of T_c was found at higher values of n. Their results indicated that the maximum value of T_c for the prepared samples of (Hg-Tl)-1223 was 125 K.

Alias *et al*.[10] prepared superconductors at high temperature with $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+δ}$ 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 ℃, whereas the sintering period was 100 h. The Tl substitution in Hg sites for $Hg_{0.6}Tl_{0.4}Ba_2Ca_2Cu_3O_{8+δ}$ 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 Tl 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 (T_c) and superconducting phase morphology of $Hg_{1-x-y}Tl_xPb_yBa_2Ca_2Cu_3O_{8+δ}$ 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 T_c 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 Tl at the Hg site on the physical properties, such as the structure, critical temperature and electrical resistivity, of $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+δ}$ 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 Hg_2O, $BaCO_3$, CaO, CuO, and Tl_2O_3, 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 $Ba_2Ca_2Cu_3O_8$ 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 calcinied 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 Hg_2O and Tl_2O_3 to obtain a nominal compound of $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$. 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 (T_c), the linear four point probe dc technique at a temperature range of (77-300) K was used.

X-ray diffractometer (XRD) (Philips) with the $Cu_{K\alpha}$ 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 ($v_{av\ Cu}$) and the density of the unit cell (ρ_m) for the specimens were estimated as was explained in previous papers [10, 14].
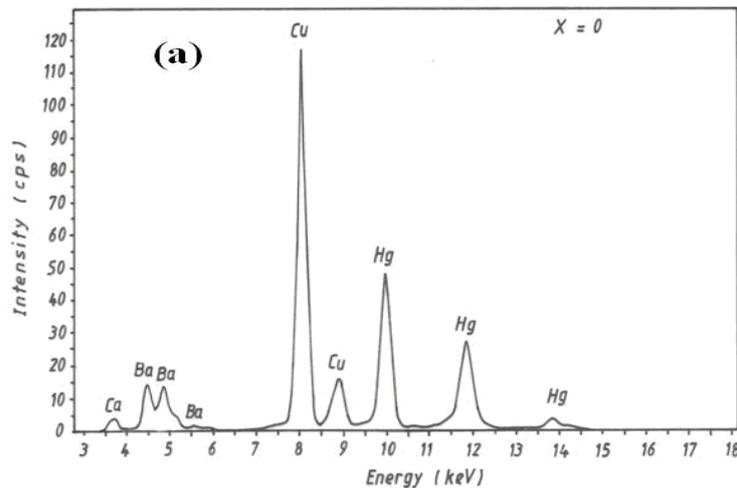
Figure 1-patterns of x-ray for fluorescent $HgBa_2Ca_2Cu_3O_{8+\delta}$ sintered in capsule.

3. Results and Discussion

The test of elements' quantities for the $HgBa2Ca2Cu3O8+\delta$ 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 $HgBa_2Ca_2Cu_3O_{8+\delta}$, which indicates the Hg-1223 high T_c phase, as a main phase, and Hg-1212 with Hg-1234 as low T_c phases, accompanied by some impurity phases like CuO and $CaHgO_2$. 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.
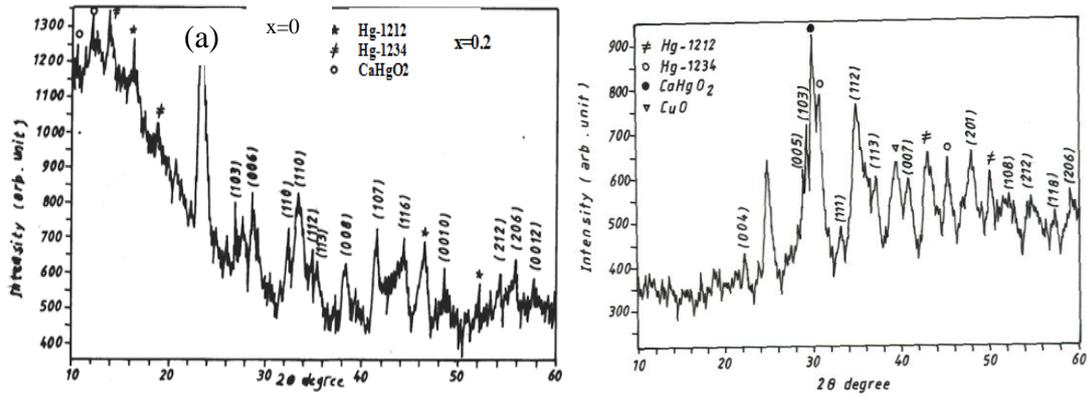
Figure 2-patterns of x-ray diffraction for (a) $HgBa_2Ca_2Cu_3O_{8+\delta}$ and (b) $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ sintered in capsule.

Table 1-Lattice constants, c/a and density ρ_m, for different composition of $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$.

x	a(Å)	c(Å)	c/a	ρ_m (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 $HgBa_2Ca_2Cu_3O_{8+\delta}$ sample has 115 K as T_c value , while 119 K is the highest T_c value of $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ .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 $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ sample had a value of 133 K which increased to 138 K after annealing in oxygen.

Furthermore, Pandey *et al.*[17] found that T_c went up when increasing Tl content of 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 T_c phases.

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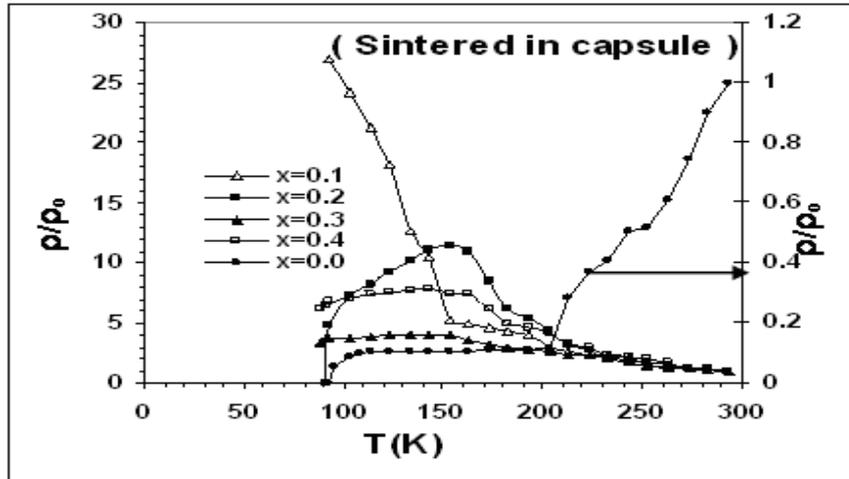
Figure 3-Normalized resistivity and temperature relation for $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$

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

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 $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ 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 $^{+2.21}$. 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 $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ 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. Putilin, S.N.; Antipov, E.V.; Chmaissem, O.; and Marezio, M.**1993**. Superconductivity at 94 K in $HgBa_2Cu0_{4+\delta}$,*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. Paviov, 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 Rahaman, 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 $Tl_{1-x}Hg_xBa_2Ca_2Cu_3O_{8+delta}$.*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 $Hg_{1-x}(Ag, In)_xBa_{2-y}Sr_yCa_2Cu_3O_{8+\delta}$* .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, $Hg_{0.5}Tl_{0.5}Ba_2Ca_{1-x}Sr_xCu_2O_{6+\delta}$, *Physica C*, **231**(1–2): 4-8.

9. Hermiz, G.Y. and AL-Beyaty,E.Kh.2011.Electrical properties of $Hg_{0.8}Tl_{0.2}Ba_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ for (n=1-5) HTSC system *Ceramic Transactions*, **226**: 129-136.

10. Alias, 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 Alias, M.F.A. 2009.Effect of Neutrons on the superconducting properties of $Hg_{1-x-y}Tl_xPb_yBa_2Ca_2Cu_3O_{8+\delta}$ for (0≤x≤0.4) and (0≤y≤0.4) System. *Iraqi j. Science,* **50**: 1636-1645.

12. Hermiz,G.Y. Alias, M.F.A. and Aljurani,B.A. **2017** .Effect of Neutrons Irradiation on the Microstructure Properties of $Hg_{1-x-y}TlxPbyBa_2Ca_2Cu_3O_{8+\delta}$ 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 $Hg_{1-x-y}Tl_xPb_yBa_2Ca_2Cu_3O_{8+\delta}$ 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 $HgBa_2Ca_2Cu_3O_{8+\delta}$ $_+$by Tl substitution *Supercon.Sci.Technol*. **10**: 218.

16. Makadsi, M.N. Hermiz, G.Y. AL-Ani, S.K. and AL-Shakarchi,E.KH. **2007**. Optimization of structure and preparing conditions of HTSC $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ 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, P. Chakoumakos, B.C. Sun, G.F. Wong, K.W. Xin, Y. Lu, D.F. **1995**. Synthesis and neutron powder diffraction study of the superconductor $HgBa_2Ca_2Cu_3O_{8+\delta}$ by Tl substitution *Physica C,* **243**: 201-206.

19. Manthiram, A. Swinnea, J.S. Sui, Z.T. Steinfink, H. and Goodenough, J.B.**198**7. The influence of oxygen variation on the crystal structure and phase composition of the superconductor yttrium barium copper oxide ($YBa_2Cu_3O_{7-x}$) *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 $HgBa_2Ca_2Cu_3O_{8+\delta}$. *Phys.Rev.B,* **51**(21): 15407-15414.