The effect of simultaneous doping of Pb in Tl-O$_\delta$ layer of Tl$_{1-x}$Pb$_x$ Ba$_2$Ca$_2$Cu$_3$O$_{9-\delta}$ superconductors

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Abstract

In this paper we have reported investigations on the effect of simultaneous substitution of Pb at the Tl-based superconductor was prepared by adding an amount of Pb to the Tl$_{1-x}$ Pb$_x$Ba$_2$Ca$_2$Cu$_3$O$_{9-\delta}$ compound. The usual solid-state reaction method has been applied under optimum conditions. Bulk polycrystalline samples have been prepared by the two-step solid state reaction process. It has been observed that the grown Tl$_{1-x}$Pb$_x$Ba$_2$Ca$_2$Cu$_3$O$_{9-\delta}$ (with x = 0.00, 0.10 , 0.20, 0.30 and 0.40) corresponds to the 1223 phase. The x-ray data of the sample showed a tetragonal structure with a high ratio of Tl-1223 superconducting phase. The samples showed a transition temperatures T$_{c(onset)}$ which were 120 K, 123 K, 129 K, 131 , 134 K at (x = 0.0, 0.10, 0.20, 0.30 and 0.40) respectively, and the transition temperatures at zero resistance T$_{c(off)}$ were 101, 105, 108, 112 and 118 K, respectively. Resistivities were measured at different temperatures under zero magnetic fields and the data were interpreted. All the samples preparation with O$_2$ flow, we found that the O$_2$ flow in our samples produced high- Phase superconductors.

X-ray diffraction analysis showed an increase of the c-axis lattice constant for the samples doped with pb as compared with these have no pb content. It was found that the change of the pb concentrations of all our samples produced a change in the density ρ_m, C/a and volume fraction V$_{Ph(1223)}$.

Introduction

The TlBa$_2$Ca$_2$Cu$_3$O$_{9-\delta}$ (1223) phase was transition temperature, T$_c$, of ,112 K the first superconducting composition to be reported among its analogs, with a superconducting (1,2). This compound is well

known as one of the Ruddelsden-Popper series of homologous compounds, $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ where n = number of Cu-O layers (3), in which an alternating structural arrangement of rocksalt and perovskite layers is found. $TlBa_2Ca_2Cu_3O_8$ is tetragonal with space group I4/mmm, a = 3.847 Å and c = 15.89 Å (4). The $TlBa_2Ca_2Cu_3O_{9-\delta}$ phase has also been studied in terms of phase equilibria (5,6), bulk processing and properties (7), and thin-film processing and characterization (8). Other high temperature superconductor members in this series include the 2212, 2223, 2234, and 1234 phases. All are potentially of commercial interest, as their T_c values (highest 125 K) are significantly higher than those of $Ba_2YCu^3O_{6+x}$ (90 K) and the Bi-Sr-Ca-Cu-O compounds (highest 110 K). Many substitutional variations of the 1223 Tl-Ba-Ca-Cu oxide phase have been studied. Matsuda et al.(9) prepared $TlSr_2Ca_2Cu_3O_6$ and found it to have a critical temperature of 100 K. Single phase $TlSr_2Ca_2Cu_3O_9$ is known to be difficult to prepare, however the liquid phase synthesis method reported by Morgan et al.(10), has led to some success. The properties and stability of the 1223 family of phases can be substantially improved by partial substitution of Pb and/or Bi for Tl in the rocksalt layer (11-12). Examples of these compositions are $Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_3O_{8.2}$ (12) and $Tl_{0.64}Pb_{0.2}Bi_{0.16}Sr_2Ca_2Cu_3O_x$ (11). The structure of $(Tl,Pb)Sr_2Ca_2Cu_3O_9$ was investigated by using neutron powder diffraction and electron microscopy (13) Most processing appears to involve a melt phase, either as a transient liquid, or as an equilibrium product. Information on melting equilibria of the 1223 phase is therefore critical for processing. Only a few studies of melting in the Tl-Ba-Ca-Cu-O and related 1223 systems have been investigated, probably due to the high volatility. Blaugher (14) reported a schematic melting diagram based on data available, but included only double thallium layer compounds. Li et al. (15) reported a peritectic melting of unsubstituted 1223 at 905 8C in oxygen. Melting products included CaO and $BaCuO_2$. In addition to melting, a major factor is the control, or monitoring, of thallia pressures during processing. Many of the "1223" systems currently of interest contain six or more components, creating a need for accurate data relating the thallia pressures to multicomponent bulk compositions. Holstein (16) measured thallia pressures over pure Tl_2O_3 This serves as a baseline with which to compare pressures in various Tl-containing systems,

and has also provided a method for control of Tl pressures, via the "two-zone" method used by Aselage and others (5). They reported a stability region for the 1223 in terms of the variables PTl2O, PO2 and temperature. A complementary approach would be to measure equilibrium pressures over 1223 as a function of temperature. Wahlbeck et al. (17) measured thallia pressures over the 2223 phase using mass spectrometry. However, thallium pressures over "1223" stoichiometries apparently have not been measured by any of these or any other methods. One of the central problems of 1223 research concerns stoichiometry. In earlier work we presented preliminary data showing nonstoichiometry of the Tl- Ba-Ca-Cu-O 2212 phase. This is undoubtedly true for 1223 as well; for example, Holstein et al. (8) have presented evidence for a range of disordered phases between 2223 and 1223. It is reasonable to suggest that many of the difficulties encountered in synthesis of single phase 1223 could be explained by compositional shifts associated with nonstoichiometry. On purely crystal chemical grounds such nonstoichiometry would be likely because of the similar ionic radii of Tl^{+1} and Ba^{+2} and of Tl^{+3} and Ca^{+2}. Any of these variations would necessarily be linked to oxygen pressure. In principle, Pb^{+2} could substitute on any of three sites, in the rocksalt layer, as well as for Ca and Ba or/and Sr, leading to further stoichiometric variations.

Experimental

The synthesis of $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$ HTSC phases (x= 0.00, 0.10, 0.20, 0.30 and 0.40) samples were prepared by sold state reaction , using appropriate weights of pure powders (99.998% from May & Baker LTD Dagenham England) materials Pb_3O_2, , Tl_2O_3, $BaCO_3$, $CaCO_3$ and CuO, and in proportion to their molecular weights.The weight of each reactant was measured by using a sensitive balance type (Mettler H35 AR with Capacity: 110 grams and Readability: 0. 001). The synthesis of the samples have been carried out by twostep precursor method. In the first step, the powders ($BaCO_3$, $CaCO_3$ and CuO) were mixed together by using agate mortar ; a sufficient quantity of 2- propane was to homogenize the mixture and to form slurry during the process of grinding for about (40-60) minute.The mixture was dried for an oven at 150^0 C.The mixture was

weighted (w_1) and put in alumina crucible.The mixture was put in tube furnace that has programmable controller type (Eurptherm 818), for calcinations, which is the heat treatment to remove CO_2 gas from the mixture. For this process the powder was heated to temperature of 800 ^0C for 24 hours with a rate of 60 ^0C /h , then cooled to room temperature by the same rate of heating. The weight of mixture after calcinations was measured (w_2), the colour of it was black. If the difference in the sample weight before and after the calcinations process (w_2-w_1) is less than the theoretical value of gas then the step above should be repeated again , and the calcined powder was reground again, for two or three times to remove the whole gases from the mixture.

In the second step, the $Ba_2Ca_2Cu_3O_7$ precursor was mixed with Pb_3O_2, Tl_2O_3 to obtain the nominal compositions $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$ where x= 0.00, 0.10, 0.20, 0.30 and 0.40. The powder was pressed into disc-shaped pellets (1.3 cm) in diameter and (0.2-0.3) cm thick, using hydraulic press type (Specac) under a pressure of 7 ton/cm^2 .The pellets were presintered in air at (855-860) ^0C for (24 h) with a rate of 60 ^0C/h and then cooled to room temperature by same rate of heating.The presintered pellets were reground, repressed and resintered in the oxygen (oxygen rate 0.3 L/min) at the same range of temperature for further 200 h and then cooled to 500 C and annealed in oxygent for 10 h and then cooled to room temperature by same rate of heating. By regrinding and resintering 1212 phase can be exposed and directly take part in the reation which can accelerate the formation rate of the1223 phase of Hg-base and produces the pure 1223 phase more easily .

The samples were examined with resistivity experiments by used standard four-probe technique to investigate their superconducting state(18). The resistivity (ρ) could be found from the relation: $\rho = \dfrac{V}{I}\dfrac{\omega t}{L}$ Where : I is the current passing through the sample. V is the voltage drop across the electrodes. ω is the width of the sample. L is the effective length between the electrodes. t is the thickness of the sample. The structure of the prepared sample was obtained by using x-ray diffractometer (XRD) type (Philips) has the following features, the source $Cu_{k\alpha}$ current (20 mA), voltage (40 KV) and $\lambda=1.5405$ A^0. Phase

transformation for many composition was studied by using XRD to get the structure properties(19). The volume fraction of any phase (V_{phase}) in the sample were determined by using the relation:

$$V_{phase} = \frac{\sum \Gamma a}{\sum \Gamma 1 + \sum \Gamma 2 + \ldots\ldots + \sum \Gamma n} \times 100.$$

Where Γa is the XRD peak intensity of the phase which were determined, $\Gamma_1, \Gamma_2, \ldots \Gamma_n$ are the peaks intensity of all XRD.

Results and discussion

All the samples in the present investigation were subjected to gross structural characterization by X-ray diffraction. The XRD data collected from various samples (samples having various Pb, Ca, Ba,Cu and Tl concentration) were all polycrystalline and correspond to Tl(Pb)-1223 phases. The XRD also shows some impurity phases with vanishingly small concentrations. The representative XRD patterns are shown in figures(1). It could be seen from the spectra that there were two main phases in all samples of the Tl-base systems, high-T_c phase (1223), low-T_c phase(1212) and a small amount of impurity phases of $(Ca, Ba)_2CuO_3$, $CaPbO_4$ and CuO. The appearance of more than two phases could be related to the stacking faults along the c-axis. The comparison between the relative intensities of XRD patterns for the samples with Pb=0.10, 0.20, 0.30 and 0.40, figure(1) with the relative intensity of the same reflections of the sample with Pb=0.0 [x=0.00] shows that all the samples have reflection intensity of the High-T_c phase reflections (peaks H), and Low –T_c phase reflections (peaks L) the H-peaks increased and Low-Tc decreased by increasing Pb. The High-T_c phase reflections of the free sample (Pb= 0) has lower intensity than samples have Pb.The lattice parameters have been estimated using d-values and (hkl) reflections of the observed x-ray diffraction pattern through the software program based on Cohen's least square method(20), the parameters a, b, c , density ρ_M and volume fraction (V_{phase}) shown in table(1).

Figures (2), (3) and(4) show an increase of the transition temperature (T_c) with volume fraction (V_{phase}) , c/a and decrease of ρ_M for Pb-doped samples for different composition of $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{8+\delta}$ as comparable with the free sample, the reason is due to the

substitution of Pb for Tl where the ionic radii of Pb^{+4} is longer than that of Tl^{+2} which renders c-parameter to be longer or get deformed.

The variation of resistance with temperature of the as synthesized $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{8-\delta}$ HTSC samples was measured by the standard four-probe technique. The normal state resistance of all the samples shows metal like behaviour with respect to temperature. A plot of the normalized resistivity vs temperature (ρ –T) behaviour of samples with various Tl concentrations are shown in figure(5). The values of critical transition temperature (T) for as grown $TlBa_2Ca_2Cu_3O_{8.789}$, $Tl_{0.90}Pb_{0.10}Ba_2Ca_2Cu_3O_{8.779}$, $Tl_{0.80}Pb_{0.20}Ba_2Ca_2Cu_3O_{8.767}$, $Tl_{0.70}Pb_{0.30}Ba_2Ca_2Cu_3O_{8.74}$ and $Tl_{0.60}Pb_{0.40}Ba_2Ca_2Cu_3O_{8.703}$, phases are 101 K, 105 K, 108 K, 112 and 118 K, respectively. In view of the quality characterization provided by A. R.N. Bhattacharya et al (21), it can be categorically stated that our samples are of 'good quality'. Since the maximum value of T_c is expected to be for optimum hole doping, the concentration $Hg_{0.80}Tl_{0.20}Ba_2Ca_2Cu_3O_{8.755}$ would correspond to optimum level of hole doping. In order to verify this, the phase corresponding to $Tl_{0.60}Pb_{0.40}Ba_2Ca_2Cu_3O_{8.703}$ was annealed in oxygen.

Conclusions

In the present study, we have investigated the effect of simultaneous doping of Pb in $Tl-O_\delta$ layer of $Tl_{1-x}Pb_x Ba_2Ca_2Cu_3O_{9-\delta}$. The as grown samples are dominantly Tl(Pb)-1223 phas. The transition temperature of as grown samples is found to be sensitive to the Pb concentrations .It has been observed that maximum Tc (118 K) is achieved for $Tl_{0.60}Pb_{0.40}Ba_2Ca_2Cu_3O_{8.72}$ wherePb =0.40 This phase does not need any additional post synthesis oxidation or reduction treatment and the as grown phase itself is optimally doped. This phase has been reproducibly produced and is very much stable and degradation in T_c is very small over a significant period.

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Table(1): Values of lattice parameter, C/a, oxygen content (δ), T_c and ρ_M for the samples for different composition of $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$

X	$T_{c(OFF)}(K)$	$T_{c(ON)}(K)$	$\delta(O_2)$	$a(A^0)$	$b(A^0)$	$c(A^0)$	C/a	ρ_M (g/cm³)	$V_{Ph-1223}$
0.00	101	120	0.211	3.839	3.838	15.82	4.120	5.5931	65.49
0.10	105	123	0.221	3.846	3.846	15.86	4.124	5.5846	67.14
0.20	108	129	0.233	3.849	3.848	15.89	4.128	5.5841	70.53
0.30	112	131	0.260	3.851	3.851	15.92	4.134	5.5787	72.98
0.40	118	134	0.293	3.854	3.853	15.96	4.141	5.5704	75.50
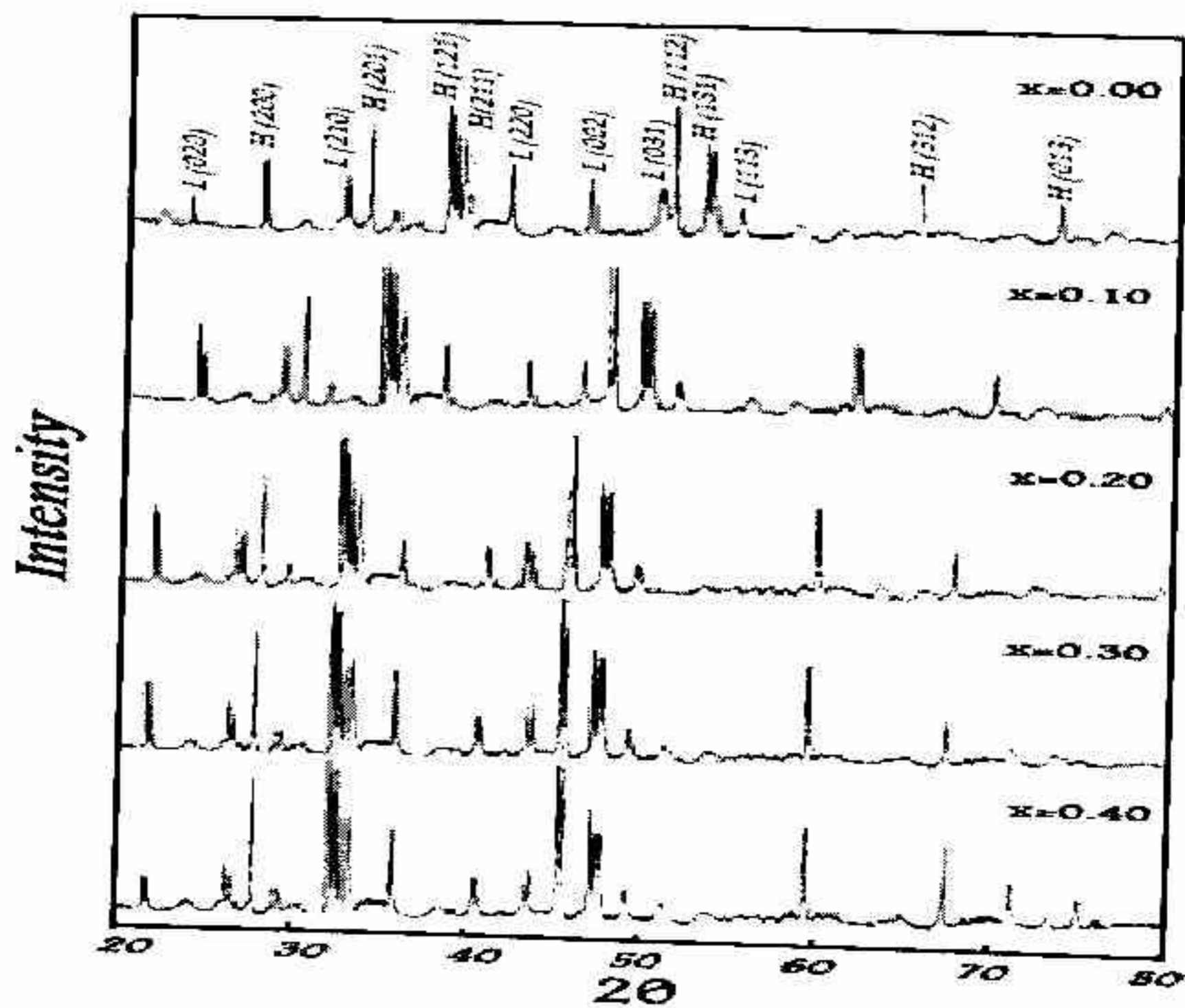
Fig(1) XRD Patterns for the sample $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$ for x=0.10, 0,20, 0.30, and 0.40
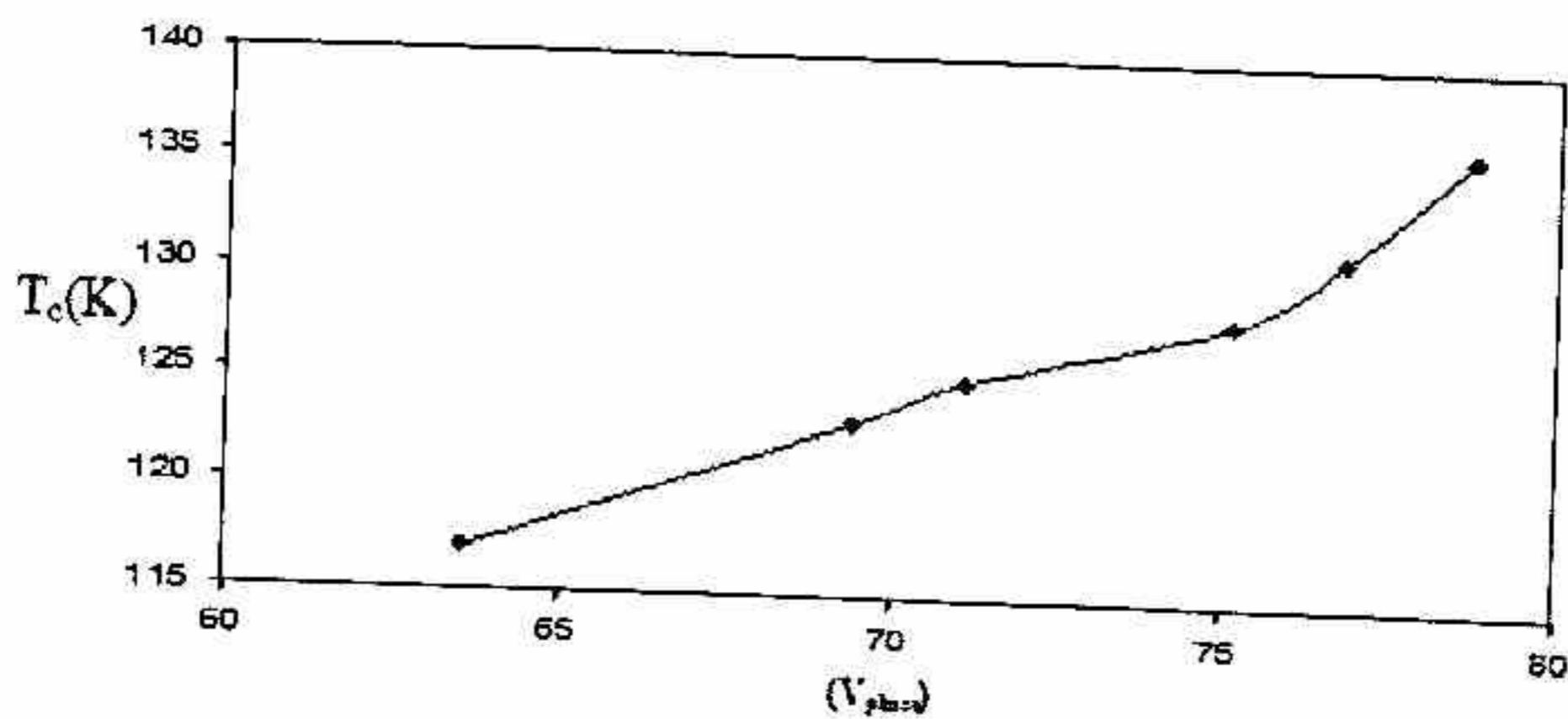

Fig.(2) Transition temperature (T_c) as function volume fraction (V_{phase}) for deferent Pb at $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$
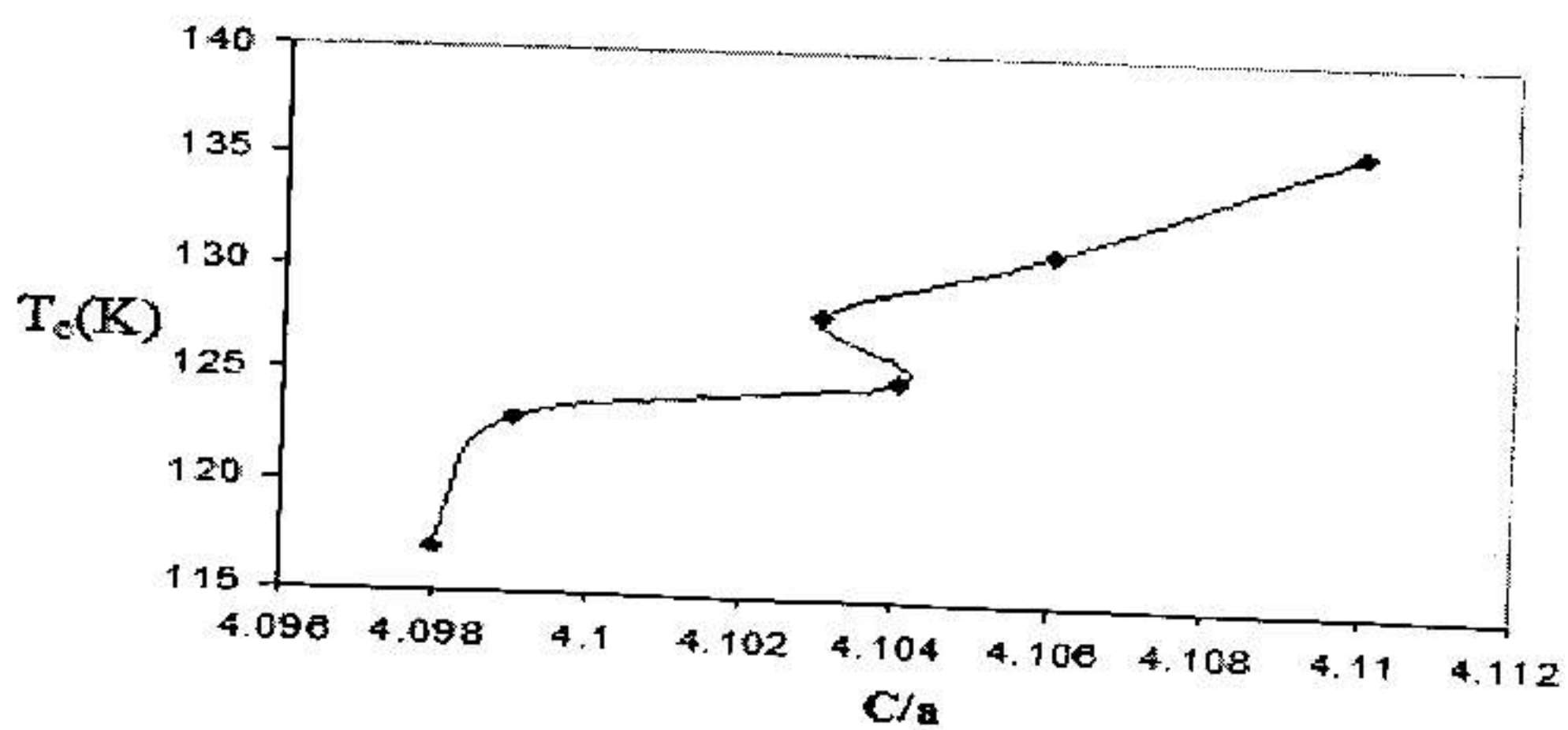
Fig.(3) Transition temperature (T_c) as function of C/a for deferent Pb at $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$
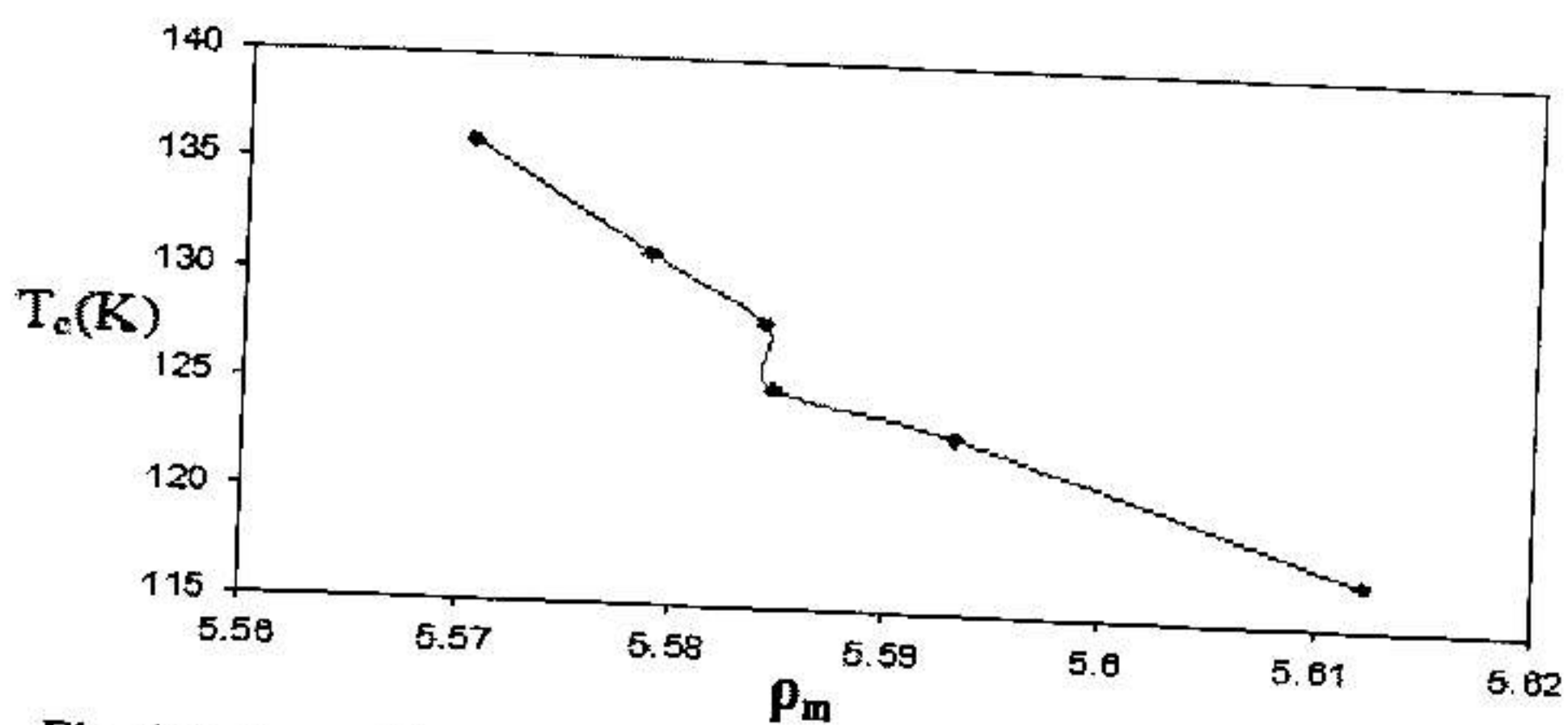

Fig. (4) Transition temperature (T_c) as functionof density ρ_m for deferent Pb at $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$
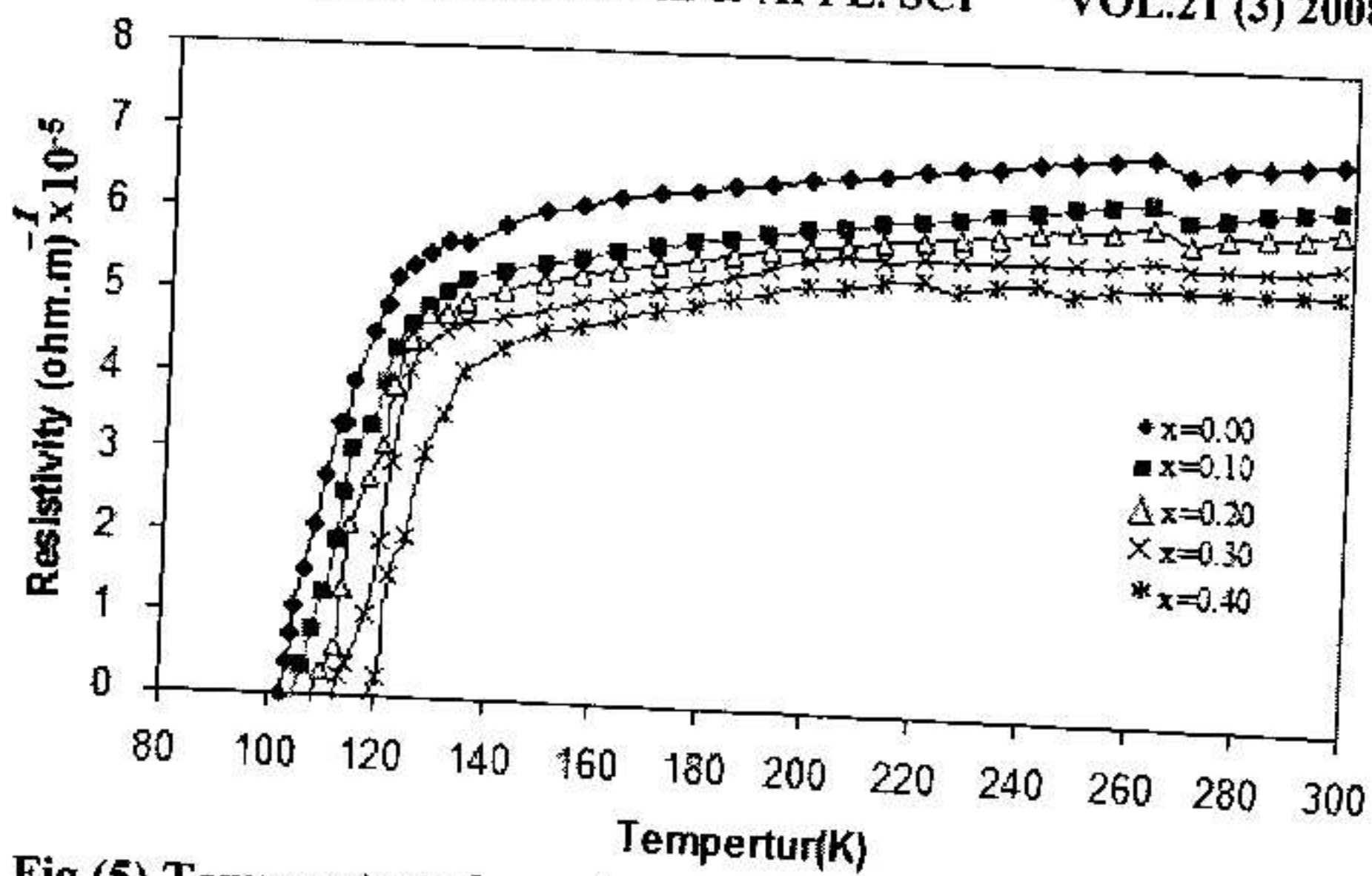
Fig (5) Temperature dependence of resistivity for $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$ at indicated values of (Pb) at   x =0.00, 0.10,   0.20 ,   0.30 and 0.40

تأثير التطعيم بالرصاص (Pb) في طبقة Tl-O في خصائص المركب الفائق التوصيل Tl₁₋ₓPbₓBa₂Ca₂Cu₃O₉₋δ

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الخلاصة

في هذه الدراسة نبين تأثير تطعيم الرصاص Pb في طبقة Tl-O فـي خـصائص مركب الثاليوم الفائق التوصيل $TlBa_2Ca_2Cu_3O_{9-\delta}$ باضافة نسب معينة من الرصاص. حضرت العينات لهذا المركب على شكل طبقة سميكة متعددة التبلورباسـتخدام خطـوتين بطريقة تفاعل الحالة الصلبة. بينت تحليلات الاشعة الـسينية أن المركبـات ذو تركيـب معيني قائم ذو نسبة عالية من الطور Tl-1223 الفائق التوصيل وأظهرت هذه التحلـيلات زيادة في قيمة الثابت C مع تغير في الكثافة ونسب الاطوار للعينات المـستخدم فيهـا الرصاص مقارنة مع الخالية منه. استخدمت تقنيـة (4 point probe) لإيجـاد درجـة الحـرارة الحرجـة T_c. وجـدنا إن قـيم لــ T_c للمركـب فـائق التوصيل $Tl_{1-x}Pb_xBa_2Ca_2Cu_3O_{9-\delta}$ هـي 134, 131, 129 K, 123 K, 120 K $T_{c(onset)}$ وعنـد المقاومة الصفرية هي 121 ,117 ,115K ,110K=$T_{c(offset)}$ للنسب (0.30 ,0.20 ,0.10 ,0.0 =x) على التوالي. جميع العينات حضرت تحت تأثير ضخ الاوكسجين الذي أدى إلى تحسين وزيادة الــ T_c.