تحضير ودراسه الخصائص التركيبية والكهربائية للمركب الفائق التوصيل $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$

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الخلاصة

حضرت مركبات الزئبق –الرصاص –الانتيموني الفائقة التوصيل ذو الصيغة $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ (x=0, 0.10 and 0.15) باستعمال ثلاث خطوات بطريقة تفاعل الحالة الصلبة. استعملت تقنية المقاومية الكهربائية (4 point probe) لإيجاد درجة الحرارة الحرجة T_c ووجدنا أن عينة المركب $Hg_{0.5}Pb_{0.5}Ba_2Ca_2Cu_3O_{8.437}$ ذاو سلوك شبه موصل بينما عينة المركب $Hg_{0.5}Pb_{0.4}Sb_{0.1}Ba_2Ca_2Cu_3O_{8.353}$ هي ذو سلوك معدني موصل لكن عينة المركب $Hg_{0.5}Pb_{0.35}Sb_{0.15}Ba_2Ca_2Cu_3O_{8.233}$ هي فائقة التوصيل ذو درجة حرارة انتقالية ($T_{c(0ff)}$) تساوي 126K . بينت تحليلات الاشعة السينية أن المركبات ذو تراكيب معينيه قائمة وأظهرت هذه التحليلات نقصان في قيمة الثابت c مع زياده نسبة الانتيموني Sb مقارنة مع الخالية منه وان زيادة نسبة الانتيموني تسبب زيادة في نسبة الطور ($V_{phase(1223)}$) ونقصان في كلا من الكثافة الكتلية ρ_M و c/a .

الكلمات المفتاحية: –المقاومية الكهربائية ،درجة الحرارة الحرجة ، تحليلات الاشعة السينية، الكثافة الكتلية

Synthesis and Study Structural and Electrical Properties of $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ Superconductors

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Abstract

Mercury-lead-antimony based superconductors with the formula $Hg_{0.5}$ $Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ (x=0, 0.10 and 0.15) have been prepared by useing three step solid state reaction processes. Electrical resistivity, using four probe technique, is used to find the transition temperature T_c. It is found from that sample $Hg_{0.5}$ $Pb_{0.5}Ba_2Ca_2Cu_3O_{8.437}$ is semiconductor , sample $Hg_{0.5}$ $Pb_{0.4}Sb_{0.1}Ba_2Ca_2Cu_3O_{8.353}$ is normal state with metallic behaviors, while sample $Hg_{0.5}$ $Pb_{0.35}Sb_{0.15}Ba_2Ca_2Cu_3O_{8.233}$ is superconducting state with critical transition temperature (T_c) is 126K. X-ray diffraction (XRD) analysis showed a tetragonal structure with decrease in the c-axis lattice constant for the samples doped with Sb as compared with these which have no Sb content. It was found that the increase of the Sb concentrations of all our samples produce an increase of the volume fraction (V_{phase}) and decrease c/a and Mass density ρ_M .
Key words:- Electrical resistivity, Transition temperature, X-ray diffraction and Mass density

Introduction

Superconductivity in the Hg-based cuprate family having the generic formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$ ([Hg-12(n-1)n], Hg-Ba-Ca-Cu-O, HgBCCO) was first reported in 1993 [1] for the n = 1 compound (Hg-1201). Shortly thereafter, a record high T_C of 133 K was reported for the n = 3 compound (Hg-1223) under ambient conditions [2]. Subsequently, it was found that T_C values in excess of 164 K could be induced in the Hg-1223 by the application of a high pressure [3]. The Hg-1223 samples are known to degrade rapidly after synthesis. In view of this, significant efforts have recently been made to improve the stability of the Hg bearing HTSC phases, particularly the Hg-1223 phase. It is now known that the most effective way to improve the stability of the Hg-1223 phase is through suitable cationic substitution for Hg. Typically suited cations are those having oxidation states higher than that of Hg^{+2} greater than + 2 such as, Tl^{+3}, Pb, Bi^{+3} , and Re[4-7] . They bring in more oxygen in the oxygen deficient HgO_δ layer leading to phase stability. The higher oxidation state cations also lead to hole optimization in the hole deficient as grown Hg-1223 phase, thus producing optimum critical transition temperature (T_c).

In the present work we have successfully prepared $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ bulk polycrystalline superconductor by using three step solid state reaction process, we have doped $Hg_{0.5}Pb_{0.5}Ba_2Ca_2Cu_3O_{8+\delta}$ with Sb taken in varying concentrations stability of Hg(Pb)-1223 phase.

Experimental

The synthesis of $Hg_{0.5}$ $Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ HTSC phases (x= 0, 0.10 and 0.15) have prepared solid state reaction method , using appropriate weights of pure powders (99.998%

from May & Baker LTD Dagenham England) materials of HgO, , Pb_2O_3, Sb_2O_3,$BaCO_3$, $CaCO_3$ and CuO. 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 three step 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 homogenization the mixture and to form slurry during the process of grinding for about (30-50) minute.The mixture was dried by an oven at (200^0 C). 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 ($800\ ^0$C) for three hours with a rate of ($200\ ^0$C /hr) , then cooled to room temperature by the same rate of heating.

In the second step, the $Ba_2Ca_2Cu_3O_7$ precursor was mixed with HgO, Sb_2O_3 and Pb_2O_3 to obtain the nominal compositions $Hg_{0.5}\ Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ where x=0.0, 0.10 and 0.15. 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 8 ton/cm^2 .The pellets were presintered in air at (855-860) ^{0}C for (8 hours) with a rate of ($200\ ^0$C/hr) and then cooled to room temperature by same rate of heating.

In the third step, the pellets were reground, repressed and resintered in the oxygen (oxygen rate 0.6 L/min) at the same range of temperature for further (12 hours) and then cooled to ($500\ ^0$C) and annealed in oxygen for (4 hours) and then cooled to room temperature by the same rate of heating. The samples were examined with resistivity experiments by using standard four-probe technique which is most common method of determining the $\underline{T_c}$ of a superconductor. The sample was fixed in the cryostat instrument which was joined to a rotary pump to get a pressure of 10^{-2} mbar inside the cryostat, and also joined to a sensor of digital thermometer (type Pt 100 resistance to temperature detection RTD) near the sample position. A 10 mA current was supplied to the sample by a current source D.C power supply type (Electronica- Veneta DV 30/V3); the voltage drop was measured by a Keithley model 180 nanovoltmeter with sensitivity of a bout ± 0.1 nanovolt was used for voltage measurements. The resistivity (ρ) could be found from the relation: $\rho = \frac{V}{I}\frac{\omega t}{L}$ 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. All measurement of L, t and ω were made by using digital vernier. The exess of oxygen content (δ) could be determined by useing chemical method called Iodometric titration.The structure of the prepared sample was obtained by using x-ray diffractometer (XRD) type (Philips) which have the following features, the source $Cu_{k\alpha}$ current (20 mA), voltage (40 KV) and λ=1.5405 A^0. A computer program was established to calculate the lattice parameters a,b,c this program is based on Cohen's least square method.The volume fraction of any phase (V_{phase}) in the sample were determined by using the relation(14):

$$V_{phase} = \frac{\sum Ia}{\sum I1 + \sum I2 + ... + \sum In} \text{x}100$$ Where Ia is the XRD peak intensity of the phase which were determined,$I_1, I_2, ... I_n$ are the peaks intensity of all XRD.

A computer program was established to calculate the lattice parameters a,b,c this program is based on Cohen's least square method[8].

Results and Discussion

The temperature dependence of the electrical resistivity(ρ) for Sb free sample and samples with different Sb contents (x=0.1 and x=0.15) in $Hg_{0.5}\ Pb_{1-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$) are shown in figure (1). It is found from this figure that the behavior of resistivity with temperature of the composition which has no Sb is semiconductor while the addition of Sb content in the $Hg_{0.5}$ $Pb_{1-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$) transform from normal state at (x=0.1) to superconducting state at

x=0.15(The value of critical transition temperature ($T_{c(off)}$) for as grown $Hg_{0.5}Pb_{0.35}Sb_{0.15}Ba_2Ca_2Cu_3O_{8+\delta}$ phases is 126K). This behavior is due to the fluctuation of oxygen excess and the increasing of Sb, while may lead to metastable structure, that decrease T_c, but most of them x=0.15, transform the structure to a stable phase. A small amount of Sb addition is quite effective in decomposing the low-T_c phase (1212) of $Hg(Pb)Ba_2Ca_2Cu_3O_{8+\delta}$ superconductor systems by producing $BaHgO_3$ and $BaCuO_2$ accompanied by high-T_c phase formation. The destruction of the low phase by Sb at the early stage may enhance the nucleation and the formation of high-T_c phase. Enhancement of free Sb will raise the resistivity and this will, much more, increase $BaPbO_3$ which is an insulator consisting of Hg-O.

The XRD data collected from various samples (samples having various Hg, Pb, Sb Ca, Ba and Cu concentration) were all polycrystalline and correspond to Hg(Pb,Sb))-1223 phases. The XRD also shows some impurity phases with vanishingly small concentrations. The representative XRD patterns are shown in figures(2). It could be seen from the spectra that there were three main phases in all samples of the Hg-base systems, high-T_c phase (1223) reflections (peaks H), and Low –Tc phase reflections (peaks L)and a small amount of impurity phases of $(Ca, Ba)_2CuO_3$, $CaPbO_4$, $CaSbO_4$ 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 Sb=0, 0.1 and 0.15, with the relative intensity of the same reflections of the sample with Sb=0 shows that all the samples have reflection intensity of the High-T_c phase reflections and Low –T_c phase reflections the H-peaks increased and Low-Tc decreased by increasing Sb . The High-T_c phase reflections of the free sample (Tl= 0) has lower intensity than samples have Sb . The lattice parameters have been estimated using d-values and (hkl) reflections of the observed x-ray diffraction pattern through the software program), the parameters a, b, c , Mass density ρ_M and volume fraction (V_{phase}) shown in table(1).Figures (3), (4), (5) and(6) show an increase of the volume fraction (V_{phase}) and decrease C, C/a and ρ_M for Hg-doped samples for different composition of $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ as comparable with the free Sb sample.

Conclusions

We have synthesis of $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ HTSC phases (x= 0, 0.10 and 0.15) have prepared solid state reaction method. It is found that the behavior of resistivity with temperature of the composition which has no Sb is semiconductor while the addition of Sb content in the $Hg_{0.5}Pb_{1-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ transform from normal state (x=0.1) to superconducting state x=0.15(The value of critical transition temperature ($T_{c(off)}$) for as grown $Hg_{0.5}Pb_{0.35}Sb_{0.15}Ba_2Ca_2Cu_3O_{8+\delta}$ phases is 126K).

The increasing of Sb leads an increase of the volume fraction (V_{phase}) and decrease c/a and ρ_M for samples for different composition of $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$.

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Table(1): Values a,b,c ,c/a, δ and ρ_M for the samples for different composition of $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$

X	$T_{c(OFF)}$(K)	$T_{c(ON)}$ (K)	$\delta(o_2)$	$a(A^0)$	$c(A^0)$	c/a	ρ_M (g/cm^3)	$V_{Ph-1223}$
0.00	------	------	0.437	3.842	15.99	4.161	5.9765	39.44
0.10	------	-------	0.353	3.844	15.91	4.139	5.7351	55.17
0.15	126	135	0.233	3.843	15.66	4.075	5.5841	75.79

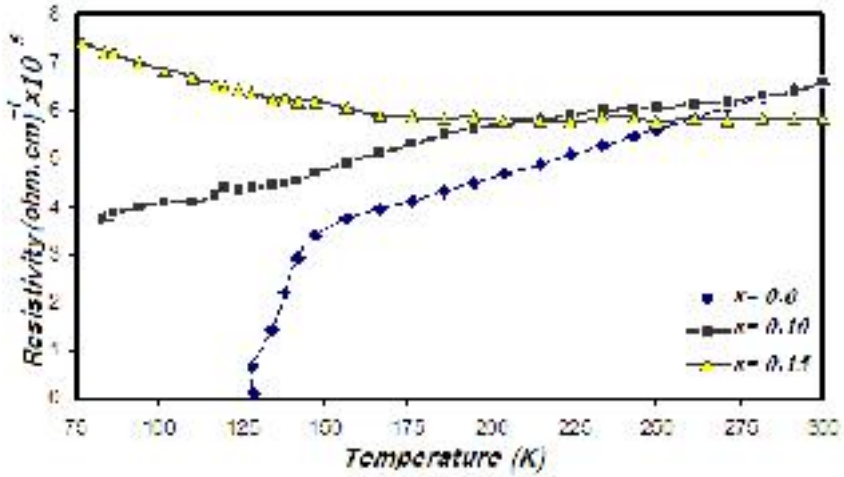
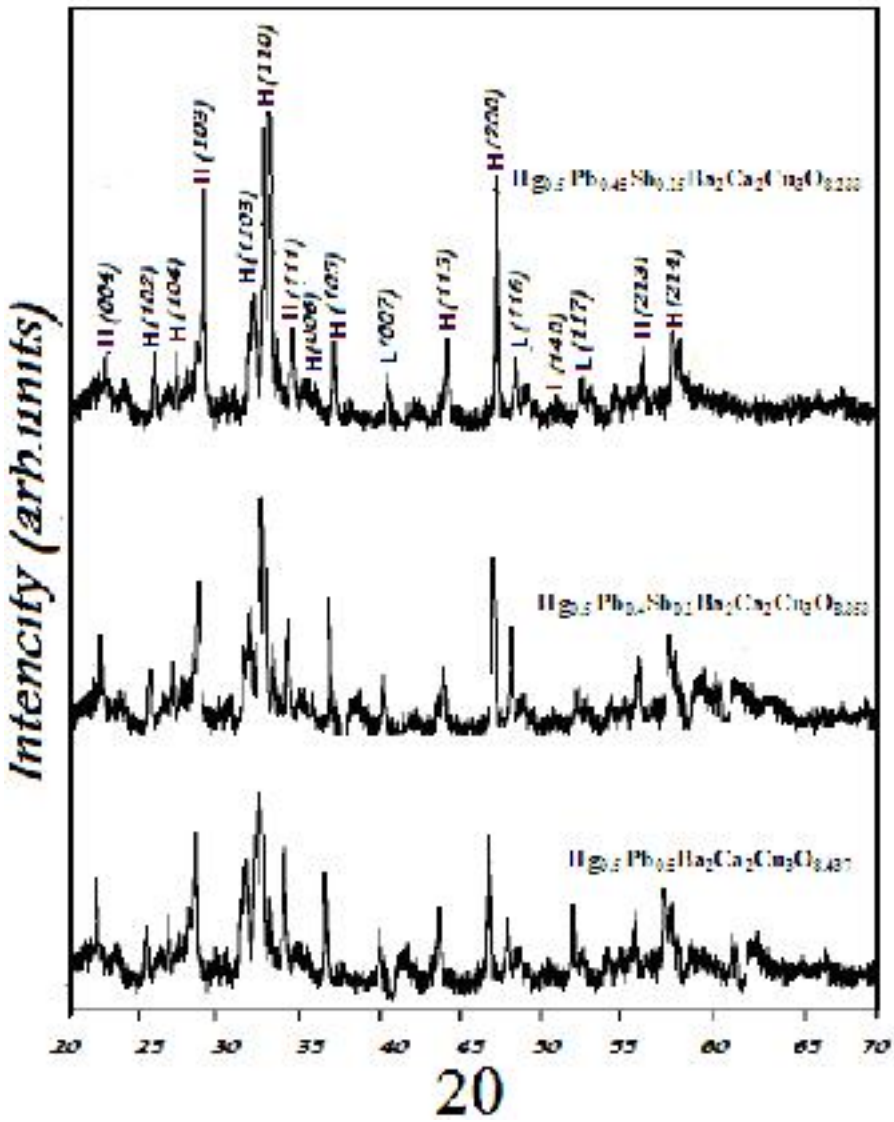


Fig. (1): Temperature dependence of resistivity for $Hg_{0.5}Pb_{1-x}Sb_xBa$ at indicated values of (Sb) at x =0.00, 0.10 and 0.15



Fig(2) XRD Patterns for the sample $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$ for x=0.00, 0.10 and 0.15

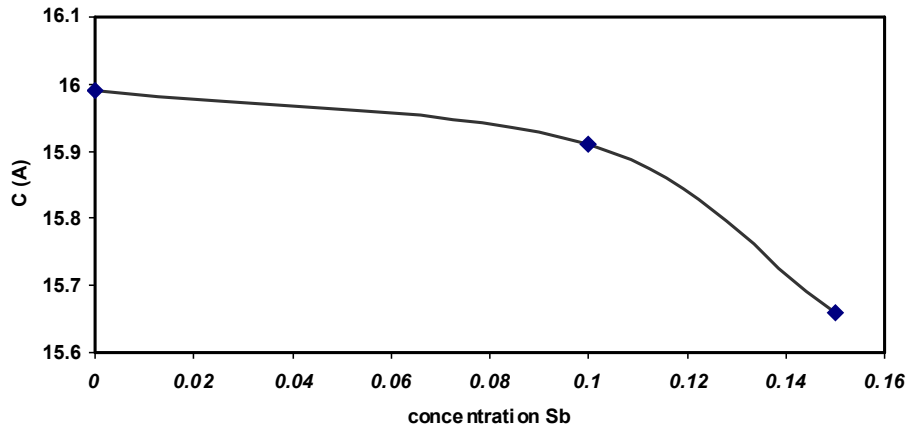


Fig.(3): parameter C as function of diferent Sb for $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$

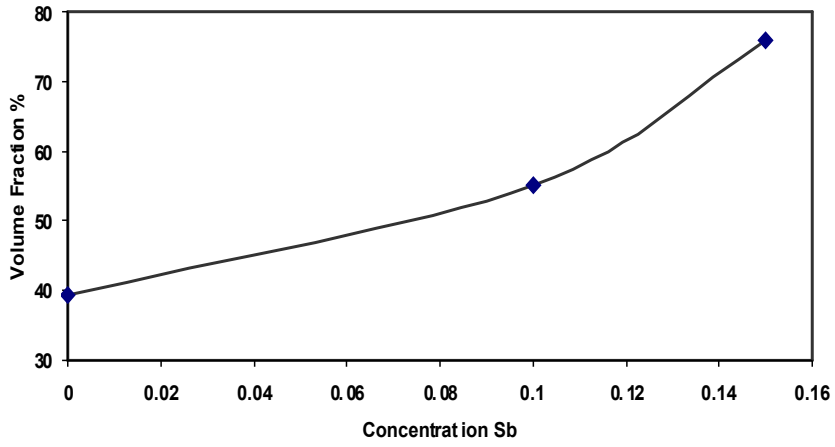


Fig.(4): volume fraction (V_{phase}) as function of diferent Sb for $Hg_{0.5}$ $Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$

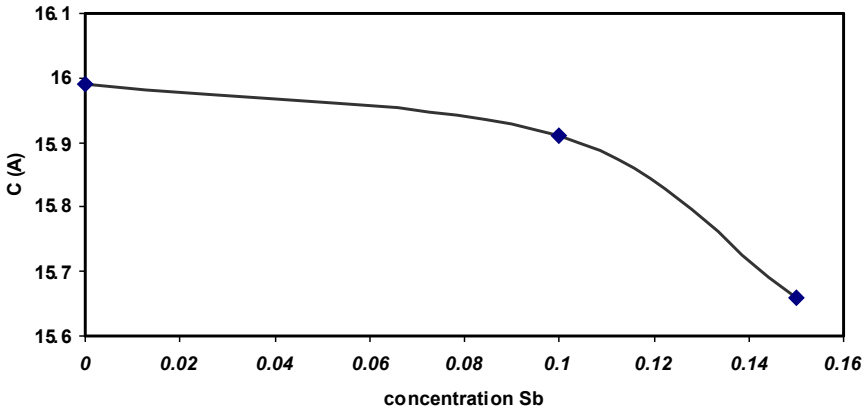


Fig. (5): C/a as function of Sb concentration for $Hg_{0.5}$ $Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$

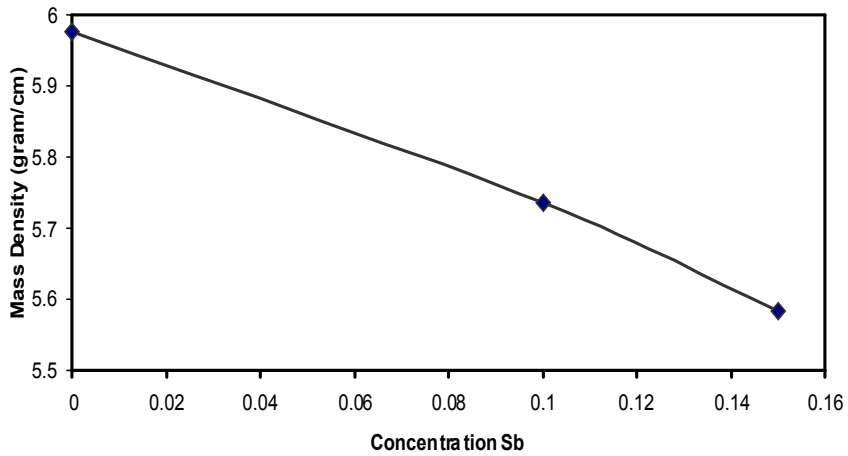


Fig. (6): Mass Density ρ_M as function of Sb concentration for $Hg_{0.5}$ $Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$