تحضير ودراسة الخصائص التركيبية والكربانية للمركب الفائق التوصيل 

Hg$_{0.5}$Pb$_{0.5-x}$Sb$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$

كرم علي جاسم، محمد عبد النبي، مصطفى محمد علي 
قسم الفيزياء، كلية التربية – ابن الهيثم، جامعة بغداد 
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الخلاصة

حضرت مركبات الزئبق-الرصاص-الانتيموني الفائق التوصيل ذو الصيغة Hg$_{0.5}$Pb$_{0.5}$Sb$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ بواسطة ثلاث خطوات بطريقة تفاعل الحالة الصلبة. استخدمت تقنية المقاومة الكربانية (4 point probe) لتجديد درجة الحرارة الحصرية T$_c$، ووجد أن عينة المركب Hg$_{0.5}$Pb$_{0.5}$Sb$_{0.1}$Ba$_2$Ca$_2$Cu$_3$O$_{8.353}$ ذو سلك معدني موصل وكان عينة المركب Hg$_{0.5}$Pb$_{0.35}$Sb$_{0.15}$Ba$_2$Ca$_2$Cu$_3$O$_{8.233}$ ذو درجة التوصيل وزها. تساوي 126K. بينت تحليلات الأشعة السينية أن المركبات ذو تراكيب معينة قائمة وأظهرت هذه التحليلات نقصان في قيمة الثابت c مع زيادة نسبة الانتيموني Sb مقارنة مع الخالية منه وإن زيادة نسبة الانتيموني تسبب انخفاض في نسبة الطرق وニックشان في كلا من الكثافة الكتلة و c/a.

الكلمات المفتاحية: المقاومة الكربانية، درجة الحرارة الحصرية، تحليلات الأشعة السينية، الكثافة الكتلة.
Synthesis and Study Structural and Electrical Properties of Hg$_{0.5}$Pb$_{0.5-x}$Sb$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ Superconductors

K. A. Jasim, M. Abdul-Nebi and M. M. Ali
Department of Physics, College of Education Ibn-Al-Haitham, University of Baghdad
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Abstract
Mercury-lead-antimony based superconductors with the formula Hg$_{0.5}$Pb$_{0.5-x}$Sb$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ ($x=0$, 0.10 and 0.15) have been prepared by using 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$_2$Ca$_2$Cu$_3$O$_{8.437}$ is semiconductor, sample Hg$_{0.5}$Pb$_{0.4}$Sb$_{0.1}$Ba$_2$Ca$_2$Cu$_3$O$_{8.353}$ is normal state with metallic behaviors, while sample Hg$_{0.5}$Pb$_{0.35}$Sb$_{0.15}$Ba$_2$Ca$_2$Cu$_3$O$_{8.233}$ 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 with 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 $\rho_M$.

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$_2$Ca$_n$Cu$_{2n+1}$O$_{2n+2}$ ([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$_{\delta}$ 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$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ bulk polycrystalline superconductor by using three step solid state reaction process, we have doped Hg$_{0.5}$Pb$_{0.35}$Sb$_{0.15}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with Sb taken in varying concentrations stability of Hg(Pb)-1223 phase.

Experimental
The synthesis of Hg$_{0.5}$Pb$_{0.5-x}$Sb$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ 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, PbO, Sb2O3, BaCO3, CaCO3 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 (BaCO3, CaCO3 and CuO) were mixed together by using agate mortar; a sufficient quantity of 2-propanol 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 °C). The mixture was put in tube furnace that has programmable controller type[Europ therm 818], for calcinations, which is the heat treatment to remove CO2 gas from the mixture. For this process the powder was heated to temperature of (800 °C) for three hours with a rate of (200 °C /hr), then cooled to room temperature by the same rate of heating.

In the second step, the Ba2Ca2Cu3O7 precursor was mixed with HgO, Sb2O3 and PbO3 to obtain the nominal compositions Hg0.5 Pb0.5-xSbxBa2Ca2Cu3O8+δ 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/cm2. The pellets were presintered in air at (855-860) °C for (8 hours) with a rate of (200 °C/hr) and then cooled to room temperature by the 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 °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 Tc of a superconductor. The sample was fixed in the cryostat instrument which was joined to a rotary pump to get a pressure of 102 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 ±0.1 nanovolt was used for voltage measurements.

The resistivity (ρ) could be found from the relation: \( \rho = \frac{V}{I \times \omega \times L} \) Where : I is the current passing through the sample, \( V \) is the voltage drop across the electrodes, \( \omega \) 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 \( \omega \) were made by using digital vernier. The excess of oxygen content (δ) could be determined by using 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 CuKα current (20 mA), voltage (40 KV) and \( \lambda = 1.5405 \) A. 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 (Vphase) in the sample were determined by using the relation(14):

\[
V_{\text{phase}} = \frac{\sum I_a}{\sum I_1 + \sum I_2 + \ldots + \sum I_n} \times 100
\]

Where \( I_a \) is the XRD peak intensity of the phase which were determined. \( I_1, I_2, \ldots, I_n \) 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 Hg0.5 Pb1-xSbxBa2Ca2Cu3O8+δ 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 Hg0.5 Pb1-xSbxBa2Ca2Cu3O8+δ 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_{0.15}Sb_{0.15}Ba_2Ca_2Cu_3O_{8+δ} 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+δ} 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 –T_c 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-T_c 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+δ} 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+δ} 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_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+δ} 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+δ} 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+δ}.

References

5. Jassim, K.A. (2005) Comparison Study of T_c Between the Superconducting Compounds Bi2-x(Hg,Pb)xSr_{2+y}Ba_2Ca_2Cu_3O_{10-δ} and Hg_{1-x}Pb_xSr_{2+y}Ba_2Ca_2Cu_3O_{8+δ}, Ph.DThesis, University of Baghdad , College of Science , Physics Dep. Iraq.

Table(1): Values a,b,c,c/a, δ and ρM for the samples for different composition of Hg0.5Pb0.5-xSbxBa2Ca2Cu3O8+δ

<table>
<thead>
<tr>
<th>X</th>
<th>Tc(OFF)(K)</th>
<th>Tc(ON)(K)</th>
<th>δ(º)</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>c/a</th>
<th>ρM (g/cm³)</th>
<th>Vp1223</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-----</td>
<td>-----</td>
<td>0.437</td>
<td>3.842</td>
<td>15.99</td>
<td>4.161</td>
<td>5.9765</td>
<td>39.44</td>
</tr>
<tr>
<td>0.10</td>
<td>-----</td>
<td>-----</td>
<td>0.353</td>
<td>3.844</td>
<td>15.91</td>
<td>4.139</td>
<td>5.7351</td>
<td>55.17</td>
</tr>
<tr>
<td>0.15</td>
<td>126</td>
<td>135</td>
<td>0.233</td>
<td>3.843</td>
<td>15.66</td>
<td>4.075</td>
<td>5.5841</td>
<td>75.79</td>
</tr>
</tbody>
</table>

Fig. (1): Temperature dependence of resistivity for Hg0.5Pb1-xSbxBa at indicated values of (Sb) at x =0.00, 0.10 and 0.15
Fig(2) XRD Patterns for the sample $\text{Hg}_{0.5}\text{Pb}_{0.5-x}\text{Sb}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ for $x=0.00$, 0.10 and 0.15

Fig.(3): parameter C as function of different Sb for $\text{Hg}_{0.5}\text{Pb}_{0.5-x}\text{Sb}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$
Fig.(4): volume fraction ($V_{phase}$) as function of different 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 $\rho_M$ as function of Sb concentration for $Hg_{0.5}Pb_{0.5-x}Sb_xBa_2Ca_2Cu_3O_{8+\delta}$