Structural and Transition Temperature of $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$ Superconductor

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Abstract

Solid state reaction technique (SSR) was used to prepare high-T_c phase in $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$ superconductors. The effect of additional Pb to $HgBa_2Ca_2Cu_3O_{8+\delta}$ was investigated. It has been found that the maximum transition temperature T_c=133K is at x=0.1.X-ray diffraction showed a tetragonal structure with an average value of c=15.816 Å. The average value of the valence of copper (v) is equal to 2.025.There is an increasing of density with the enhancement of the concentration of Pb.

Introduction

One of the highest temperature superconducting cuprates (HTSC) which has an inherent potential for practical application is the family of mercury-based copper oxide superconductors which have a transition temperatures above 130 K [1]. But the viability of high-temperature superconductors for many applications will ultimately depend on the size of the current density, J_c that they are able to support, not only at high temperatures, but also in high magnetic fields [2].

One of the most important factors relating to the doping mechanism of Hg superconductors is an interstitial oxygen defect in the Hg plane and cation substitution in the Hg sites. The Hg plane is deeply related to the doping [3].

Doping with various elements was found to be useful and effective in improving the properties of HTSC, different cation substitutions for Hg,e.g.Pb,in the Hg-1223 phase have been reported to be effective for the enhancement of Hg irreversibility field characteristic and stabilize the Hg-1223 phase [4,5]. Stabilize superconductive phases, may increase the transition temperature and can introduce more oxygen in the crystal structure.

The difficulty on the synthesis of Hg-1223 compound is the low thermal stability and to be decompose before melting. More attention has been focused on the synthesis of (Hg-Pb) – 1223 because lead can reduce the melting temperature [3].

Watanabe et. al.[6] reported that substituting Hg partly with Pb increased considerably the amount of excess oxygen in the $(Hg,Pb)O_3$ charge –reservoir block .lead was found to enter the phase with an oxidation state higher in average than III so as to

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increase the positive charge at the Hg site. However, the increase in the oxygen content counter –balanced the effect of higher –valent ($Pb^{III/IV}$) for lower –valent (Hg^{II}) cation substitution.

Wu et.al.[7] reported that Pb ionic radius scales linearly not only wiyh the lattice parameters, but also with the superconducting transition temperature. They prepared the (Hg,Pb)-1223 at atmospheric pressure with T_c=135K and δ =0.45.

Samples of $Hg_xPb_yBa_2Ca_2Cu_3O_{8+d}$ (1223) with x = 1.0, 1.2, 1.4 and y = 0, 0.1, 0.2, 0.3 were prepared by solid state method. The T_c of undoped 1223 was about 111 K. After annealing in oxygen the T_c increased to 133 K. The T_c for Pb-doped samples depended slightly on the Pb-content, for the as-prepared specimens were generally higher than for undoped specimens and additional annealing did not significantly change the T_c[8].

In this paper we studied the superconducting properties of $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$ HTSC system as a function of Pb for the different composition to obtain the optimum condition of substitution yielding the highest T_c.

Experimental

Solid –state reaction method was used to prepare samples of $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$ for different values of x. Powders of CaO, CuO and $BaCO_3$ and Pb_3O_4were mixed together using agate mortar.A sufficient quantity of 2-propane was used to homogenization the mixture. The mixture was grounded to a fine powder and then calcined in air at 800°C for 20 h in two stages. The calcined powder was regrind again after the mixing it with HgO and 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 sintered in an oven of temperature of 850°C at air environment for 200h with a rate of 4°C/min. in a tube furnace (in the intermediate process of sintering, the samples were cooled to 350°C for five hour in order to stabilize the phase), after this, the samples were cooled to room temperature by the same rate of heating .The samples were examined by Meissner effect to evaluate the superconducting state. The structure of the prepared samples was obtained by using x-ray diffractometer (XRD) type (Philips) with the $Cu_{K\alpha}$ source. To measure the resistivity (ρ) and to find the optimum transition temperature (T_c), four probe dc method at temperature range (77-300) K was used. .Iodometric titration was used to access the oxygen content (δ) in the samples.

Results and Discussion

X-ray diffraction patterns for the Pb-free samples and the samples with different additional values of Pb to the $HgBa_2Ca_2Cu_3O_{8+\delta}$ system is shown in figure (1). The peak positions and intensities of the diffraction data revels that our samples mainly consist of Hg-1223 and a small amount of 1212 as a minor phase together with some other unidentified peak ,that may be due to $CaHgO_2$ or $BaCuO_2$ as referred by Akao *et.al.*[4] and by Kawai *et. al.* [9] respectively . Hg-1223 are indexed as shown in Fig.(1).The lattice parameters of the existing Hg-1223 phases in our samples were calculated by a computer program which is based on Cohen's least square method .The results obtained were listed in Table (1). We found from this Table and figures (2) &(3) a decreases of the lattice constant (c),(a) and the volume (V) in the range value of Pb 0-0.2 after then there is

an increases till the value that make the composition like a semiconductor i.e .Pb is equal to 0.5 . The average value of c is equal to 15.816 A° which is in comparable value of c=15.9 A° as referred by I.Kirschoner et.al[10]

where: $c=9.5+3.2\,(n-1)$

n=3 in this search depending on the general formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$

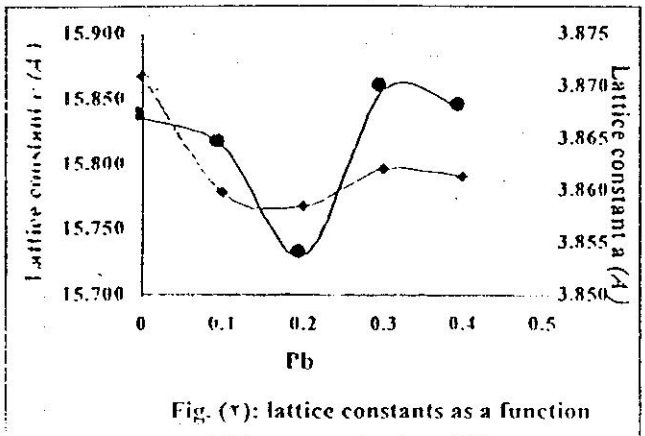

Fig. (٢): lattice constants as a function of the concentration of Pb.

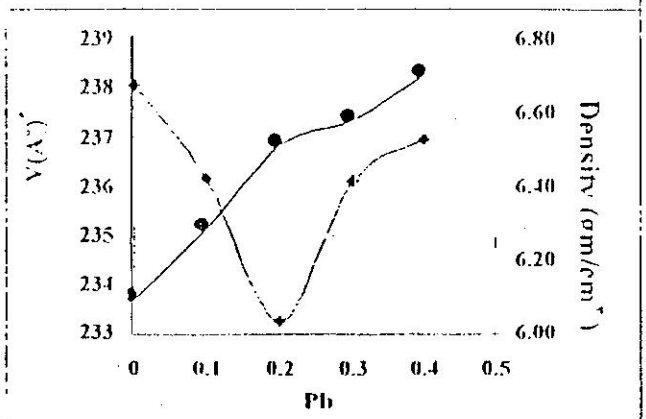

Fig. (٣): Variation of volume cell and the density as a function of the concentration of Pb.

Table (1): Values of the lattice constant, volume cell and density of different Pb concentration.

Pb	a(A°)	c(A°)	V(A°)³	c/a	Density (d) gm/cm³
0	3.871	15.835	238.102	4.091	6.095
0.1	3.865	15.813	236.19	4.092	6.289
0.2	3.851	15.729	233.289	4.084	6.515
0.3	3.859	15.858	236.149	4.109	6.582
0.4	3.868	15.843	236.982	4.096	6.704
0.5	Semiconductor				
0.6	Semiconductor				

Density of the superconductor system at different concentration of Pb are listed in Table (1) and shown in figure (3) this could be found as referred in the previous paper [11]. We found increases of the density with the enhancement of the concentration of Pb, this means a decreases of the porosity and vacant in the system.

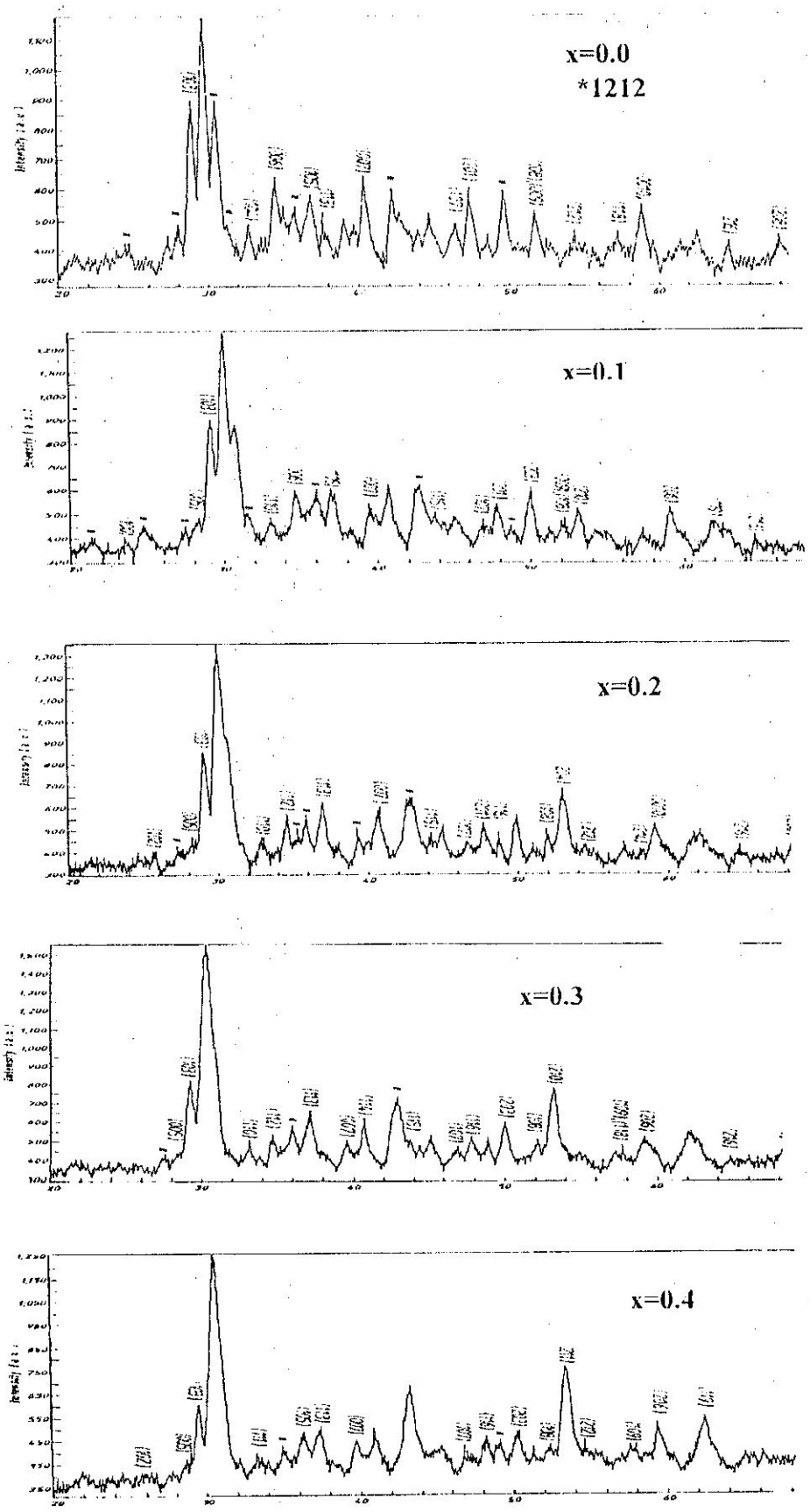

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Fig (1) X-ray diffraction patterns of $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$ for the samples with different value of x.

The amount of excess oxygen, δ, was analyzed with idometric titration for all the samples. As referred by Watanabe et. al.[6] that Pb enters the Hg-1223 phase with an oxidation state higher than III in average. Additions of Pb to the composition will increase the positive charge at the charge reservoir cation site concomitantly the oxygen content increases as reveled from the results of idometric titration for the composition $HgPb_{0.1}Ba_2Ca_2Cu_3O_{8+\delta}$ in comparison with the $HgBa_2Ca_2Cu_3O_{8+\delta}$ composition. An excessive addition of Pb (0.2-0.6) will produce decreases of the oxygen content as shown in figure (4) and Table (2). Beside of the lead effect another effect play an important role in the variation of positive charge which is the valence of copper (v) of the homologous series in question which could be calculated from the relation [10].

$v = 2(n+\delta)/2$

Which is more than two in the superconducting samples and this value decrease with the enhancement of lead content which effect (decreases), in our opinion to the value of the positive charge. The average value of v in our samples is equal to 2.025.

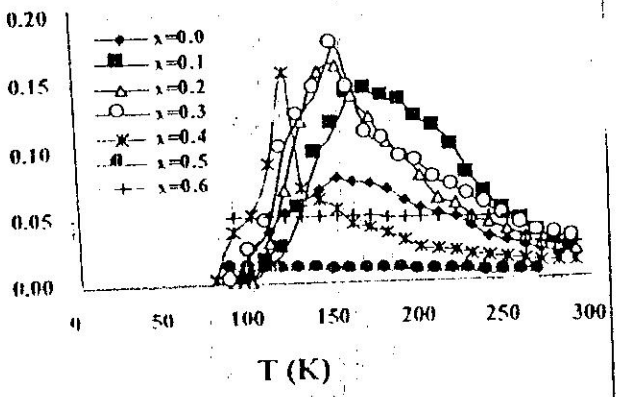

Fig. (5) Temperature dependence of resistivity for $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$

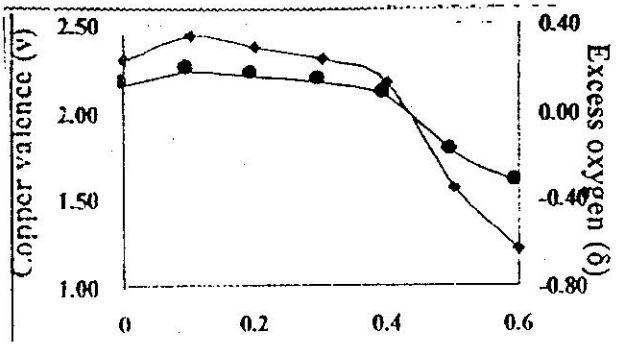

Fig (4)

Fig. (5) shows the temperature dependence of the electrical resistivity (ρ) for Pb free samples and samples with different Pb contents of (x = 0.1, 0.2, 0.3, 0.4,0.5,0.6) in $HgPbxBa_2Ca_2Cu_3O_{8+\delta}$. It is found from this figure that the behavior of resistivity (ρ) with temperature for the compositions with x = 0.5 and 0.6 is semiconductor, while the resistivity of the other composition in this research decreases with decreasing temperature i.e. the behavior is superconductor in the approximately rang 150K to 80K. The samples behave like a semiconductor between 300-150 K. Also we found there is a slight displacement to the low temperature when the turning is occurring.

Table (2): Values of the transition temperature Tc , excess of oxygen(δ), Valence of Cu (v) for different Pb concentration.

Pb	Tc (K)	Excess of Oxygen(δ)	Valence of Cu (v)
0	118	0.235	2.157
0.1	133	0.344	2.229
0.2	123	0.295	2.197
0.3	118	0.242	2.161
0.4	98	0.132	2.088
0.5	Semiconductor	-0.350	1.767
0.6	Semiconductor	-0.631	1.579

For the composition that has no lead content the superconducting transition temperature is equal to 118K. This value increases to 133K for the composition that has 0.1 of Pb. As the value of Pb increases, the transition temperature decreases until the sample behaves like a semiconductor as shown

in Table (2) and Fig. (6). to interpret the above results we suggest that a certain amount of Pb play a good role to increase the reaction of the high T_c phase. While excessive Pb addition promotes another reaction to produce the $CaPbO_4$ phase, which is likely to assist the formation of the low – T_c phase instead of the HTP.

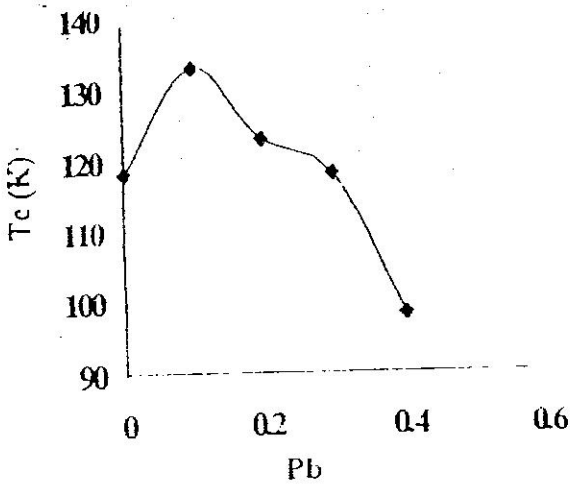

Fig. (٦): Variation of the transition temperature as a function of the

Conclusions:

It has been found that the behavior of the system $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$ with x=0-0.4 are superconductor while other samples (x >0.4) are semiconductor. Also the transition temperature T_c =133K is the maximum at x=0.1. X-ray diffraction showed a tetragonal structure with decreases of the lattice constant a and c and cell volume in the range value of Pb 0-0.2 after then there is an increase of these value till that makes the composition like a semiconductor i.e .Pb is equal to 0.5. We found increases of the density with the enhancement of the concentration of Pb, which means a decreases of the porosity and vacancy in the system.

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تركيب ودرجة الحرارة الحرجة للمركب $Hgpb \times Ba_2Ca_2Cu_3O_8$ +S الفائق التوصيل

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الخلاصة

استخدمت طريقة تفاعل الحالة الصلبة لتحضير المركب $HgPb_xBa_2Ca_2Cu_3O_{8+\delta}$ الفائق التوصيل.ودرس تأثير إضافة الرصاص للمركب . لوحظ أن أعلى درجة حرارة حرجة T_c=133K عندما تكون نسبة الرصاص مساوية إلى 0.1 . بينت تحليلات الأشعة السينية أن المركب ذو تركيب رباعي tetragonal وان معدل ثابت الشبيكة c =15.816 A° . ومعدل تكافو النحاس مساوي إلى2.025 .كما لوحظ زيادة الكثافة مع زيادة نسبة الرصاص .