Effect of isovalent substitution and Quenching on the Transition Temperature of $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

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Abstract

A high T_c superconductor with a nominal composition $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ for $(0 \le x \le 0.5)$ and $(0 \le y \le 0.5)$ was prepared by a solid state reaction method. The effect of the substitution of Pb for Bi and Ba for Sr and quenching temperature on the superconductivity has been investigated to obtain the optimum conditions for the formation and stabilization of the high T_c phase (2223).
The results showed that the optimum sintering temperature for the pure composition is equal to 875°C and the sintering time is equal to 240h with heating and cooling rate of 60°C/h . Our results indicated that a small amount of (Ba = 0.1) could raise the transition temperature (T_c), but enhancing Ba to 0.4 has raised the resistivity and the behavior of the composition converted to semiconductor and ultimately for the composition that has (x = 0.4, y = 0.5) was an insulator. The best value of (T_c = 122 K) is for the composition that has x = 0.2, y = 0.1.On the other side for Ba free samples increasing of lead content up to 0.3 has rise the transition temperature (T_c = 116 K) but more increases to (0.4, 0.5) causes a decrease in T_c.
The effect of quenching temperature T_q on the transition temperature T_c of the $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ was also investigated .It is found that all the samples have a superconductor behavior when the quenching temperature is less than 900 °C (with increase or decrease of T_c within a certain range around a sintering temperature) and they loss their superconductivity and converted to semiconductor when T_q > 900 °C.

تأثير التعويض الجزيئي والتبريد الفجائي على درجة الحرارة الأنتقالية لـ $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

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الخلاصه

حُـضرّت المركبّـات $Ca_2Cu_3O_{10+\delta}$ $(Sr_{1-y}Ba_y)_2$ الفائقـة التوصـيل ولقـيم $(Bi_{1-x}Pb_x)_2$ $(0 \le x \le 0.5)$ و $(0 \le y \le 0.5)$بطريقـة تفاعـل الحالـة الـصلبة.لقـد تمـت دراسـة تـأثيرات التعـويض الجزئـي للبزمـوث بالرصـاص، والسترونتيوم بالباريوم، كما درست أيضاً تأثيرات درجة حرارة التبريد الفجائي T_q لغرض الحصول على الظروف المثالية لتكّون واستقرار الطور الفائق التوصيل ذو درجة الحرارة الحرجة العالية (2223).
لقد بينت نتائجنا أن ظروف التلبيد المثلى للمركب النقي هي درجة حرارة تلبيد T_s تساوي 875 درجة مئوية وبفترة زمنية 240 ساعة وبمعدل تبريد وتسخين مساوي إلى (60) درجة لكل ساعة.وتشير نتائجنا إلى أن التعويض بـ 0.1 من الباريوم بالبزموث يعمل على رفع درجة الحرارة الحرجة T_c وعند زيادة قيمة Ba إلى 0.4 فإن قيمة المقاومة سوف تزداد ويتحول المركب من فائق التوصيل إلى شبه موصل وأخيراً إلى عازل للمركب الذي يحتوي على 0.5 من الباريوم و 0.4 من الرصاص. وان أفضل قيمة للدرجة الحرارية الحرجة T_c كانت مساوية إلى 122 كلفن للمركب الذي يحتوي على 0.2 من الرصاص و 0.1 من الباريوم. من ناحية أخرى، للعينات الخالية من الباريوم فأن زيادة نسبة الرصاص لحد 0.3 يعمل على رفع الدرجة الحرارية الحرجة لحد (116) كلفن، ومع زيادة نسبته لـ (0.4, 0.5) يلاحظ انخفاض في قيم T_c.
ودُرست أيضاً تأثيرات درجات حرارة التبريد السريع على درجة الحرارة الحرجة $(Bi_{1-x}Pb_x)_2$ $(Sr_{1-y}Ba_y)_2$ $Ca_2Cu_3O_{10+\delta}$ وقد لوحظ أن جميع العينات لها توصيلية فائقة عندما تكون درجة حرارة التبريد السريع T_q أقل من

900 °C (مع زيادة أو نقصان في قيمة T_c بالمقارنة مع قيمتها الأصلية)، كما أن هذه العينات تفقد موصليتها الفائقة وتتحول إلى شبه موصل عندما T_q > 900 °C.

Introduction

Since the discovery of Bi – Sr – Ca – Cu – O by Maeda *et al.* [1] has been a flurry of activity into the preparation and study of these new materials. It has become clear that their physical properties depend greatly not only on the elemental composition but also on the details of the preparation method.

Ishida *et al.*[2] quenched the $BiSrCaCu_2O_\delta$ specimens from various elevated temperature (200 – 860) °C to liquid nitrogen. From the analysis of x – ray they found that the structure is tetragonal and the lower T_c as well as the higher T_c vary remarkably but differently as a function of a quenching temperature T_q.

Che *et al.* [3] investigated the effect of quenching on the superconductivity and oxygen content of Bi(Pb) – 2223 phase. Their results indicated that the relation between $T_{c\ (0)}$, oxygen content and quenching temperature is non – linear and the heat treatment in the range of (500 – 600) °C is advantageous to improve oxygen content and $T_{c\,(0)}$.

Zhao *et al.* [4] studied the effect of liquid-nitrogen (LN_2) quenching on the phase transformation and critical current density of (Bi,Pb)-2223/Ag tapes . Their results indicate that the LN_2 quenching can effectively accelerate the increment of the (Bi,Pb)-2223 phase .

Endo *et al.* [5] have showed that the solid – state reaction under low oxygen pressure yields the pure high – T_c phase. Also, the partial substitution of Pb for Bi[6] or the addition of Pb to the composition of $Bi_2Sr_2Ca_2Cu_3O_\delta$[7] effectively stabilizes the high – T_c phase, increasing the volume fraction of this phase and lowering the optimum firing temperature to produce the high T_c – phase.

In this paper we investigated the effect of quenching on the transition temperature of $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\square}$ for (x= 0,0.1,0.2,0.3,0.4), (y = 0,0.1,0.2,0.3). Also we studied the superconducting properties as a function of Pb and Ba for the different composition to obtain the optimum condition of substitution yielding the highest T_c.

Experimental

The samples were fabricated first by calcination the mixture of Bi_2O_3, $Sr(NO_3)_2$,$CaCO_3$,CuO,Pb_3O_4 and $BaCO_3$with nominal composition of $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ for (x=0,0.1,0.2,0.3,0.4 and 0.5) at 800 °C for (24 –30) hr in two stages. The calcinad powder was reground again and pressed into disc– shaped pellets.The pellets were sintered in air at (860– 875) °C for 100 hr with a rate of 60° C/hr in a tube furnace and then cooled to room temperature by the same rate of heating. The presintered pellets were reground and repressed and resintered in air at the same range of temperature for (0 – 140) hr and then cooled to room temperature with the same rate of the first stage The pellets were examined by Meissner effect to evaluate the superconducting state. Phase transformation for composition was studied by using quenching technique for the samples at different temperatures through the heat treatment and then immersing in liquid nitrogen, the structure would be frozen. Four probe technique was used in order to find the resistivity (ρ) and to determine the critical temperature

Results and discussions

The temperature dependence of the electrical resistivity (ρ) for Ba free samples and samples with different Ba contents of (y = 0.1, 0.2, 0.3, 0.4) in $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ for (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) are shown in Figs. (1-6)). It is

found from these figures that the behavior of resistivity (ρ) with temperature for the compositions with[(x = 0, y = 0.4), (x = 0.1, y = 0.3) , (x = 0.2, y = 0.4), (x = 0.3, y = 0.4) and (x = 0.4, y = 0.2, 0.3)] is semiconductor while the resistivity of the other composition in this research decreases with decreasing temperature, although in some cases a complete zero – resistance could not be observed.

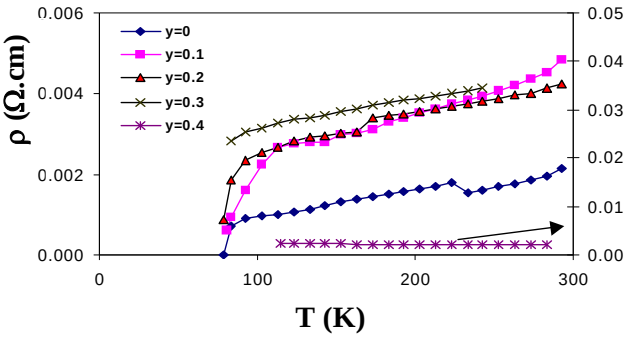


Fig. (1) Temperature dependence of Resistivity for $Bi_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

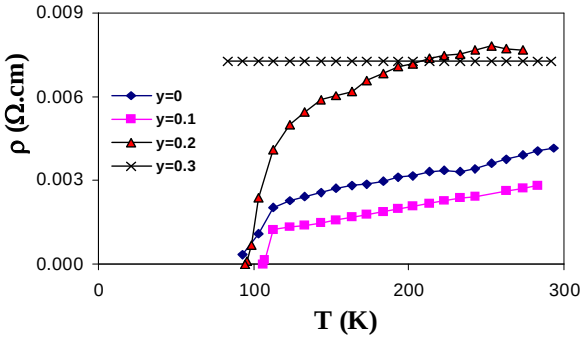


Fig. (2):Temperature dependence of Resistivity for $(Bi_{0.9}Pb_{0.1})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

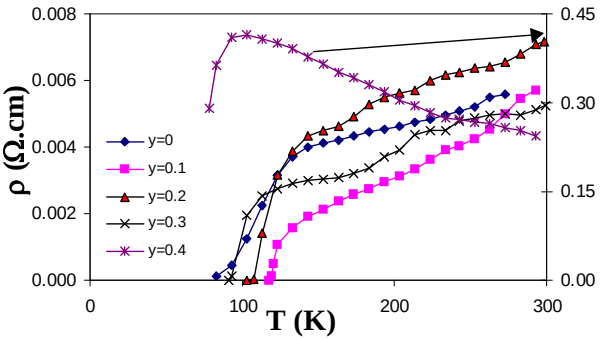


Fig. (3):Temperature dependence of Resistivity for $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

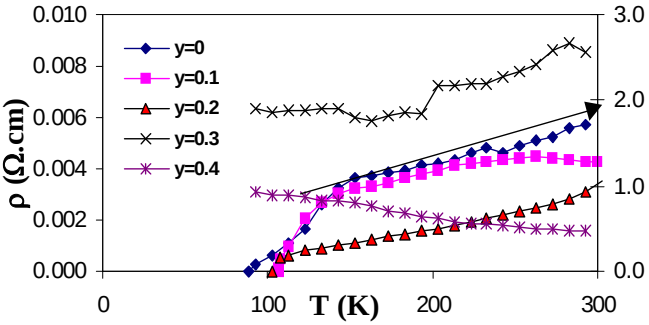


Fig. (4):Temperature dependence of Resistivity for $(Bi_{0.7}Pb_{0.3})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

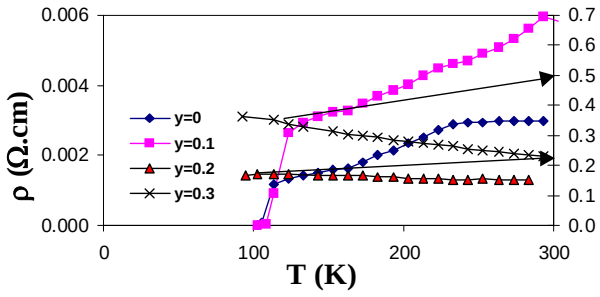
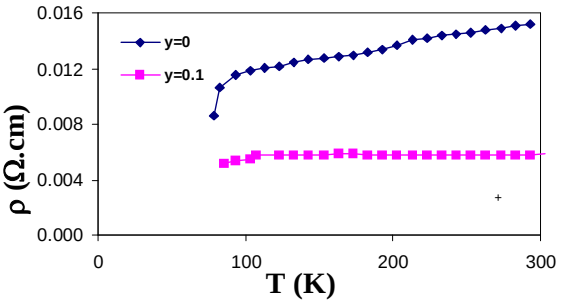


Fig. (5):Temperature dependence of resistivity for $(Bi_{0.6}Pb_{0.4})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$



Fig(6) : Temperature dependence of resistivity for $(Bi_{0.5}Pb_{0.5})(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

For the composition that has no barium content and (Pb = 0.1, 0.2, 0.3) the superconducting transition were not sharp and they had the tails around (80 – 85) K and the transition temperature (T_c) is equal to (94, 104, 116) K respectively as shown

in Figs. (2,3& 4).The reason may be attributed to the existence of small amounts of the secondary phase and/or fluctuation of the oxygen content. More addition of Pb will decrease T_c to 108 K, as shown in Fig. (7) and when Pb= 0.5 see Fig. (6), our apparatus could not help us to obtain the value of $T_{c(off)}$ because it is less than the boiling point of liquid nitrogen.

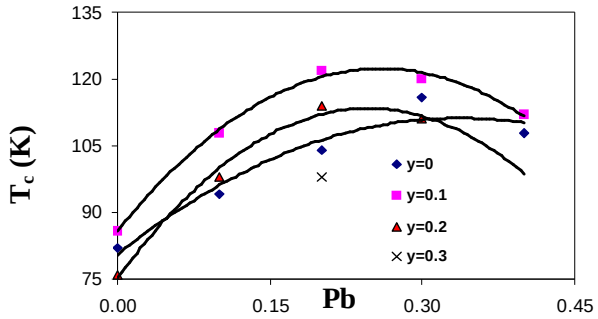


Fig. (7) : Relation of transition temperature with lead content for different value of Ba

To interpret the above results we suggest that the Pb has a catalytic effect on the reaction to form the HTP(high T_c phase). However, a certain amount of Pb is necessary for the occurrence of this reaction, while excessive Pb addition promotes another reaction to produce the $CaPbO_4$ phase [8, 9], which is likely to assist the formation of the low – T_c phase instead of the HTP. Indeed the amount of Pb suitable for the formation of the HTP is determined by the competition between these reactions A sharp drop of resistivity was observed for the composition that has (Ba = 0.1, 0.2) for different value of Pb and the composition $(Bi_{0.8}Pb_{0.2})_2(Sr_{0.7}Ba_{0.3})Ca_2Cu_3O_{10+\delta}$ as shown in Figs. (1-5).

It is found from Fig. (7) that the addition of 0.1 Ba content to the composition of different Pb content raised the transition temperature T_c and more addition (y = 0.2, 0.3) decrease the critical temperature, much more addition (y = 0.4) produce a semiconductor behavior and ultimately an insulator for (y = 0.5, x = 0.4). The results could be explained as follows:

A small amount of Ba addition is quite effective in decomposing the low – T_c phase (2212) of Bi – Sr – Ca – Cu – O superconductor systems by producing $BaBiO_3$ and $BaCuO_2$ accompanied by high – T_c phase formation as referred by Kawai *et al.*[10]. It has been reported that the low – T_c phase of double Cu – O layers strongly prohibits the formation of high – T_c phase.

The destruction of the low phase by Ba at the early stage may enhance the nucleation and the formation of high – T_c phases. Enhancement of Ba to (0.4 and 0.5) will raise the resistivity and this will, much more, increase $BaBiO_3$ which is an insulator consisting of Bi(III) and Bi(V)[11].

The resistivity behaviors as a function of temperature for quenched samples at different temperature are shown in Figs. (8-13). The quenching temperature for the studied samples have been chosen as a consequence of the DTA curve (which means a thermokinetics reaction), i.e., the peak of phase transformation in DTA spectra. It is found from these figures and Table (1) that the samples with different compositions have stayed or maintained their superconductor behavior when T_q < 900°C however, there is an enhancement or a reduction of the high transition temperature (T_c). There are two possible conduction paths in the quenching samples, but carriers may be different from each other (holes are supplied from the $(BiO)_2$ layer to the CuO_2 double layers. As a counteraction, electrons are left on the $(BiO)_2$ layers.

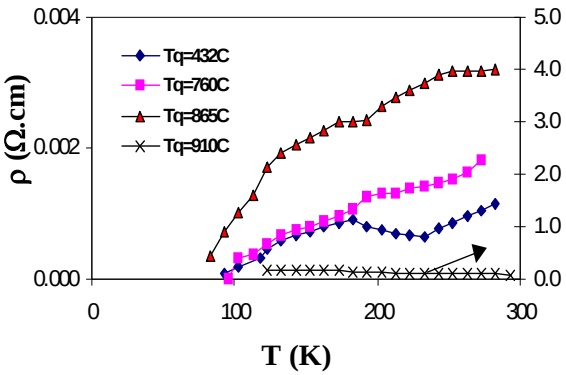


Fig. (8) : Temperature dependence of Resistivity for $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ with different quenching temperature

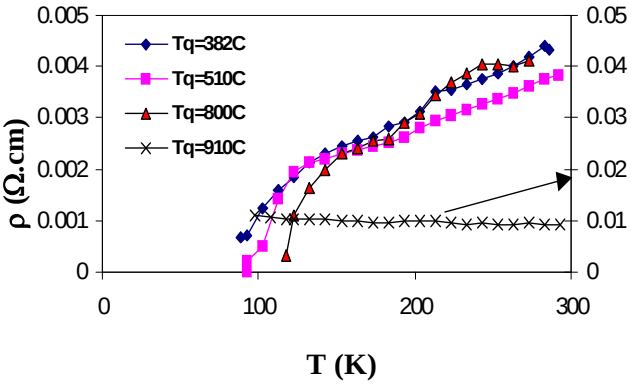


Fig. (9):Temperature dependence of Resistivity for $Bi_2(Sr_{0.9}Ba_{0.1})_2Ca_2Cu_3O_{10+\square}$ with different quenching temperature

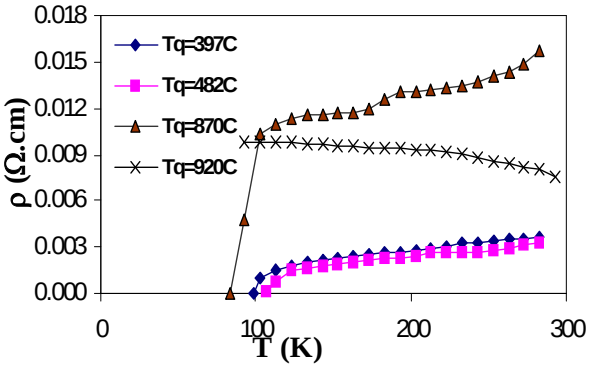


Fig. (10) :Temperature dependence of Resistivity for $(Bi_{0.8}Pb_{0.2})_2Sr_2Ca_2Cu_3O_{10+\square}$ with different quenching temperature.

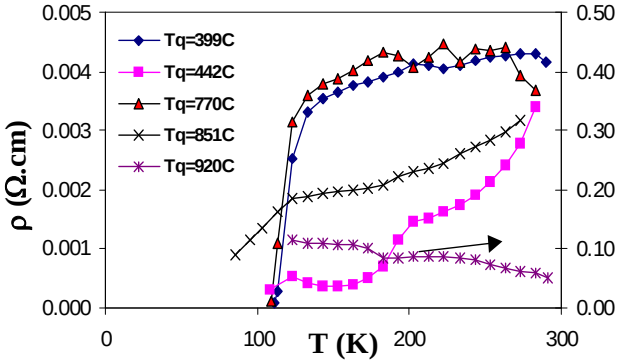


Fig. (11):Temperature dependence of Resistivity for $(Bi_{0.8}Pb_{0.2})_2(Sr_{0.9}Ba_{0.1})_2Ca_2Cu_3O_{10+\square}$ with different quenching temperature.

It might be a subtle displacement of constituent atoms that frozen by a rapid quenching from high temperature. The atomic displacement adjusts the amount of charge transfer from the Bi layer to Cu layer, and hence the changes of Tc through the hole concentration of the CuO2 plane.

It can be seen from Table (1) that for barium free samples when the quenching temperature is less than 400 °C, quenching has no effect on T_c, while there is an increases of T_c when T_q > 400 °C for (x = 0, 0.2 and 0.3) and T_q = 800 °C for (x = 0.4), the same behavior was observed for the lead free samples when T_q > 500 °C.

It is not easy to understand the enhancement of T_c with T_q, however we present two possible interpretations:

*Such T_c variations are inherent to the quenched structure that could be considered as a metastable state leading, in general to higher or lower T_c phases depending on x and y – values.

*The higher and lower T_c phases are microscopically interacted presumably through the proximity effect.

For other samples there is a deterioration of the transition temperature when $T_q \geq$ 400 °C and there is an improvement of T_c when $T_q \geq$ 770 °C for samples that has [x = 0.2, y = 0.1, 0.3] and sample with (x = 0.3, y = 0.2).

All the above specimens showed decreases of the critical temperature when the quenching temperature is greater than 850 °C, this may be attributed to the enhancement of the low – T_c phase (2212)

and at such high temperature, oxygen content took place leading to a reduction in carrier concentration.

Another feature is observed in the Ba free sample, with x = 0.2 that quenched at (397, 482 and 870) °C and with x = 0.3 that quenched at (439 and 867) °C, yield disappearance of the tails that was observed in the unquenched samples, this in our point of view is due to a more homogeneity of the samples.

The samples lost their superconductivity and converted to semiconductor when T_q > 900 °C, similar behavior was observed by Hayashi *et al.* [12]. This behavior could be explained as follows : It has been known that the (Bi, Pb) – 2223 phase decompose at high temperature as : (Bi, Pb) – 2223 → (Sr, Ca)$_2$CuO$_3$ phase + liquid phase.

Where the liquid phase has a composition between the 2212 and 2201 phase, the later is acting like a semiconductor.The presence of the liquid phase can promote the formation of the 2201 phase, but is unfavorable to the 2212 phase[13]

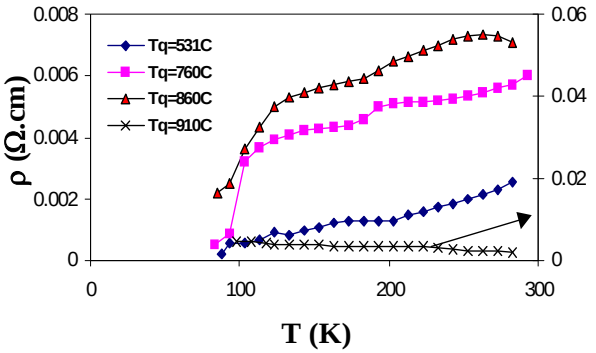


Fig. (12) : Temperature dependence of Resistivity for $Bi_2(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{10+\delta}$ with different quenching temperature

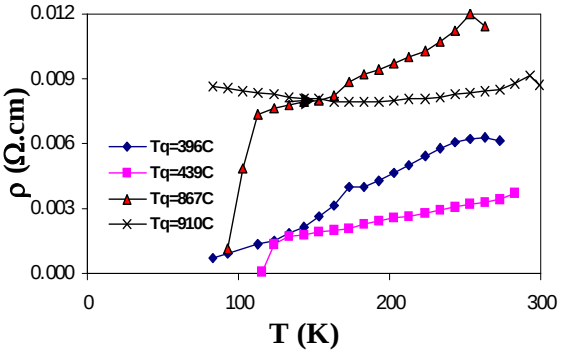


Fig. (13) : Temperature dependence of Resistivity for $(Bi_{0.7}Pb_{0.3})_2Sr_2Ca_2Cu_3O_{10+\delta}$ with different quenching temperature

Table (1) : Values of T_c for quenched and unquenched samples for different composition of $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

	y	T_q(°C)	T_c(K)	x	y	T_q(°C)	T_c(K)
0	0	un	82	0.2	0.3	Un	98
		432	92			430	80
		760	99			776	106
		865	80			856	-
		910	semi			900	Semi
0.2	0	un	104	0.1	0.1	Un	108
		397	100			810	110
		482	110			860	100
		870	90			890	86
		920	semi			910	Semi
0.3	0	un	116	0	0.1	Un	85
		396	116			382	85
		439	118			510	100
		867	100			800	118
		910	semi			910	Semi
0.4	0	un	108	0	0.2	Un	76
		371	108			531	86
		800	118			760	94

		859	-			860	-
		910	semi			910	Semi
0.2	0.1	un	122	0.3	0.2	Un	112
		399	121			399	112
		442	106			448	106
		770	116			770	120
		851	80			861	107
		920	semi			920	Semi
0.2	0.2	un	114				
		439	-				
		760	102				
		860	-				
		910	Semi				

Conclusions:

- It has been observed from the resistivity measurements that increasing of the lead content will enhance the transition temperature. However a maximum T_c value for the Ba free sample is obtained for the composition $(Bi_{0.7}Pb_{0.3})_2Sr_2Ca_2Cu_3O_{10+\delta}$ (T_c=116K). Further introduction of Pb caused a decrease in T_c ,for the composition with x=0.5, T_c is less than the boiling point of liquid nitrogen .
- The substitution of Ba in $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ superconductor has the effect of decomposing the low-T_c phase, by producing $BaBiO_3$, BaCuO2 and the high-T_c phase. A small amount of (Ba=0.1) raises the transition temperature [the best is for (Ba=0.1,Pb=0.2) where T_c = 122K]. Addition of Ba as much of (y > 0.3) for $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ results in the formation of large amounts of $BaBiO_3$ and $BaCuO_2$, which increase the resistivity and convert it at first to semiconductor and eventually an insulator.
- Phase transformation study gives evidence that the $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ systems stay maintaining their superconducting behavior when the quenching temperature is less than 900 °C and all the samples losses their superconductivity when T_q > 900 °C.

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