Optimization of structure and preparing conditions of HTSC $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ to Obtain the Highest T_c

M.N.Makadsi, G.Y.Hermiz, S.K.AL-Ani, E.KH.AL-Shakarchi*

Department of Physics, College of Science, University of Baghdad. Baghdad-Iraq.

***Department of Physics, College of Science, University of Al-Nahrain. Baghdad-Iraq.*

Abstract

High temperature superconductors with a nominal composition $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ for y equals to (0,0.1,0.2,0.3,0.4) were prepared by a solid state reaction method .The effect of sintering time ,sintering temperature, oxygen content and barium addition on the superconductivity has been investigated to obtain the optimum conditions for the formation of the high T_c phase (2223).

It has been found that a small amount of (Ba=0.1) raises the transition temperature from 80 to 122K while when Ba equal 0.3 there is a decrease of Tc to 98K, and for Ba equals 0.4 its resistivity increased the behavior of the composition converts to semiconductor.

X-ray diffraction showed an orthorhombic structure with an increase of cell volume and the peaks of the high-Tc phase for the samples doped with Ba as compared with that has no barium content.

Scanning electron microscopy has been used to evidence the morphology of the superconducting phases .The microstructures are characterized by thin elongated grains with no preferred orientation.

الخلاصة

حضرت المركبات $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ الفائقة التوصيل ولقيم y (0, 0.1, 0.2, 0.3, 0.4) بطريقة تفاعل الحالة الصلبة.

لقد تمت دراسة تأثيرات التعويض الجزئي للسترونتيوم بالباريوم, كما درست ايضاً تأثيرات زمن ودرجة حرارة التلبيد T_s ومحتوى الاوكسجين لغرض الحصول على الظروف المثالية لتكون واستقرار الطور الفائق التوصيل ذو درجة الحرارة الحرجة العالية (2223).

لقد وجد ان التعويض بـ 0.1 من الباريوم يعمل على رفع درجة الحرارة الحرجة Tc من 80 كلفن الى 122 كلفن وعند زيادة قيمة Ba الى 0.3 فأن Tc تقل الى 98 K ولقيمة Ba مساوية الى 0.4 فان قيمة المقاومة سوف تزداد ويتحول المركب من فائق التوصيل الى شبه موصل.

بينت تحليلات الاشعة السينية ان المركب ذو تركيب معيني واظهرت هذه التحليلات زيادة في حجم الخلية كما يلاحظ زيادة في القمم التي تعود الى الطور الفائق التوصيل العالي (2223) للعينات المستخدم فيها باريوم مقارنة مع تلك الخالية من الباريوم.

لقد استخدم المجهر الالكتروني الماسح لملاحظة تشكيلة الاطوار الفائقة التوصيل. ويتميز التركيب المجهري بوجود الحبيبات الطويلة وباتجاهات مختلفة.

Introduction

Since the first report of superconductivity above 30K in La-Ba-Cu-O system (1) and the following discovery of superconduction in Y-Ba-Cu-O system with T_c around 90K by many researchers (2) ,an enormous amount of works have already been reported on the so-called high $-T_c$ superconducting oxides super conductivity in the Bi-Sr-Cu-O- O system was first reported for $Sr_2Bi_2Cu_2O_{7+\delta}$ where T_c 's in the range (7-22) K were observed (3).

Maeda et al (4) have discovered a new superconductor of the $BiSrCaCu_2O_{10+\delta}$ abbreviated (BSCCO) with Tc about 105K. These oxides contain no rare earth element and have greater chemical resistance against moisture (5).

The working temperature of a superconducting device must be least 25% lower than its T_c .So yttrium series have too low T_c for liquid nitrogen temperature cooling devices. On the other hand , thallium is rather toxic its handling is thus delicate .The bismuth series do not present such disadvantage Bi-based superconductors have there superconducting phases described by a general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ (n=1,2,3). The desirable phase is the n=3 phase ,$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (2223) because of its higher T_c (7).

Unlike the thallium –system, $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (2223) is still difficult to synthesize in pure form. The reason is that the formation of the 2223 phase is very slow process and takes place within a very limited temperature range, more over, the weak bonding along the c-axis may also contribute to its stronger propensity to form intergrowth products. Sumiyama et al (8) found that the addition of surplus Ca and Cu to the ideal composition of the high $-T_c$ promotes the formation of the high T_c phase .Endo et al (9) have shown that the solid –state reaction under low oxygen pressure yields pure phase .Endo *et al* (9) have shown that the solid – state reaction under low oxygen pressure yields pure high $-T_c$ phase .Also ,the partial substitution of Pb for Bi (10) or the addition of Pb to the composition of $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (11) effectively stabilizes the high -T_c phase, increasing the volume fraction of this phase and lowering the optimum firing temperature to product the high T_c- phase .Ono(12) demonstrated that a small quantity of solidified liquid phase, special bulk composition, special temperature and long heating times become the important factors to obtain high T_c phase. To obtain a high quality pure of high T_c phase Feng *et al* (13) pointed out that it is important to divide the sintering process into two steps.

Kawai *et al* (14) reported that the addition of Ba have the effect of decomposing the structure of the 2212 phase and enhancing the high-T_c phase formation. They used the composition with excess Cu as compared with the ideal 2223 composition, the result was forming only the low-T_c phase when Ba was not added.

According to Halim *et al* (15) the Ba doping at the Ca sites does not enhance the T_c zero but gradually decreases its value from 104 K to 88K for Ba equal (0 to 0.1) respectively. Similar behavior of T_c was observed by Komatsu *et al* (16) when they doped higher percentage of barium to the composition , $Bi_{1.6}Sr_{0.4}Ca_{2-x}Ba_xCu_3O_{10+\delta}$ (x=0,0.2,0.6,1).

Bunescu *et al* (17) studied the morphology of BSCCO superconducting ceramic produced by freeze drying technique and they found that the best quality pellet, as regards the microstructure, porosity and homogeneity was obtained from that sintered for 23h at 840°C..According to the above literatures data there are contradictions in the results as coming from different laboratories.

In this paper we studied the effect of Ba addition, sintering time and sintering temperature on the transition temperature and the morphology of $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ where (y=0,0.1,0.2,0.3 and 0.4),to find optimum conditions for the highest T_c.

Experimental

The samples were prepared by solid –state reaction .Appropriate amounts of the powder materials Bi_2O_3,$Sr(NO_3)_2$,$CaCO_3$,CuO,PbO_4 and $BaCO_3$ were mixed together, after this ,the materials were grounded to a fine powder and then calcined in air at 800°C for (24-30) h in two stages .The calcined powder was regrind again and pressed into disc-shaped pellets .The pellets were sintered in air at 850-865 °C for (100h) with a rate of 60°C/h in a tube furnace and then cooled to room temperature by the same rate of heating .The presintered pellets were regrind and repressed and resintered in air at the same range of temperature for (0-140) h and then cooled to room temperature with the same rate of the first stage .By regrinding and resintering the residue 2212 phase is exposed and directly take part in the reaction which accelerates the formation rate of the 2223 phase and thus produces the pure 2223 phase more easily .The pellets were examined by Meissner effect to evaluate the superconducting state . Iodometric titration was used to find the oxygen content (δ) in the samples. Four probe dc method at temperature range (77-300) K was used to measure the resistivity (ρ) and to determine the critical temperature (T_c) . The resistivity (ρ) could be found from the expression :

ρ = RA/L

Where
R is the resistance.
A is the area of the sample.
L is the effective length between the electrodes.

The structure of the prepared samples was obtained by using x-ray diffractometer (XRD) type (Philips) with the Cu_{Ka} source .A computer program has been used to calculate the lattice parameters, which is based on Cohen's least square method.

Scanning electron microscope (SEM) type JEOL JSM 6400 was used to study the nature of grains and to analyze the surface morphology of the samples.

Results and Discussion

In order to clarify the effect of sintering time (t_s) on the electrical resistivity and the transition temperature (T_c) , the prepared samples of nominal composition $(Bi_{0.8}Pb_{0.2})_2$ Sr_2 $Ca_2Cu_3O_{10+\delta}$ and$(Bi_{0.8}Pb_{0.2})_2$ $(Sr_{0.9}Ba_{0.1})_2Ca_2Cu_3O_{10+\delta}$ were sintered at different times and the results are shown in figures (1) ,(2). It is found from these figures and table (1) that the prolonged sintering time to 240h has raised the transition temperature to 104K and 122K for the Ba free sample and sample with Ba=0.1 respectively .To interpret these results, we can see from the first sight from table (1) that there is a decrease of oxygen content as the sintering time increases, the reduction of oxygen may offer excess point defects and then group together into defect clusters, or even extended defects, such as staking faults, which may facilitate the nucleation of of the high _T_c phase and raising the transition temperature. Another reason is that during the sintering process there is an enhancement of the growth of the high T_c phase through contact areas between grains.

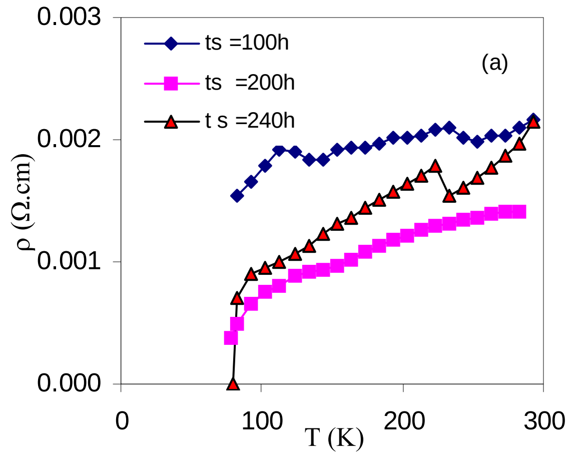


Fig. (1): Temperature dependence of resistivity for $(Bi_{0.8}Pb_{0.2})_2Sr_2Ca_2Cu_3O_{10+\delta}$ sintered at 860 °C for various periods of time in air.

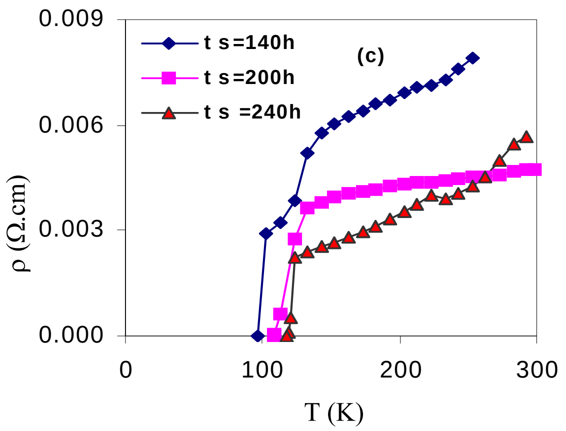


Fig.(2) : Temperature dependence of resistivity for $(Bi_{0.8}Pb_{0.2})_2(Sr_{0.9}Ba_{0.1})_2Ca_2Cu_3O_{10+\delta}$ sintered at 860 °C for various periods of time in air.

The effect of sintering temperature (T_s) on the electrical resistivity (ρ) and the transition temperature as can be seen from figure (3) that the resistivity of the composition $(Bi_{0.8}Pb_{0.2})_2(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{10+\delta}$ sintered at 850°C and 860 °C decreases nearly linearly with decreasing temperature, while that for the sample sintered at 865 °C showed semiconductive behavior.
The maximum temperature reduces to 855 °C for the composition $(Bi_{0.8}Pb_{0.2})_2(Sr_{0.7}Ba_{0.3})_2Ca_2Cu_3O_{10+\delta}$ because the behavior of resistivity with temperature was semiconductive when the sintering temperature was equal to 860 °C as shown in figure (4). At Ts =850 °C there is a

decrease in the transition temperature (complete zero – resistance could not be observed so far in our apparatus).In general, at temperature above 860 ^{o}C the resistivity behavior were bend or twisted indicating that the samples have melted partially (some of them are completely melted).

Therefore, the sintering temperature is considered to be critical for the growth of high-T_c phase and the optimum temperature seems to be close to the partial melting point.

From the above results, it is obvious that the optimum sintering temperature seemed to decrease with increasing Ba concentration.This will enhance the diffusion of the entities required for the formation of the high-T_c phase by creating a liquid phase. Figure (5) shows that the composition that has no barium content has tailings yielding a T_{czero} around 80K while , a sharp drop of resistivity was observed for other composition with (y=0.1,0.2,0.3).

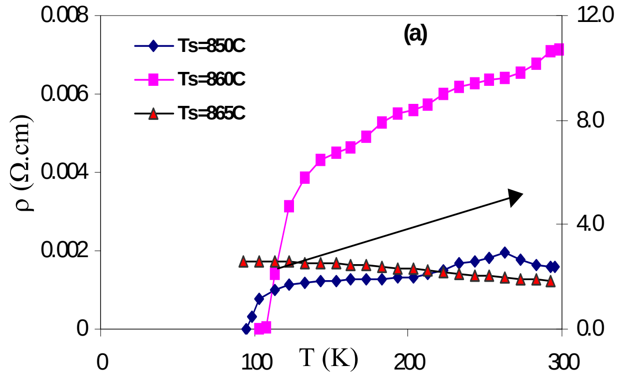


Fig. (3): Temperature dependence of resistivity for $(Bi_{0.8}Pb_{0.2})_2(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{10+\delta}$ sintered at different temperature for 240 h in air.

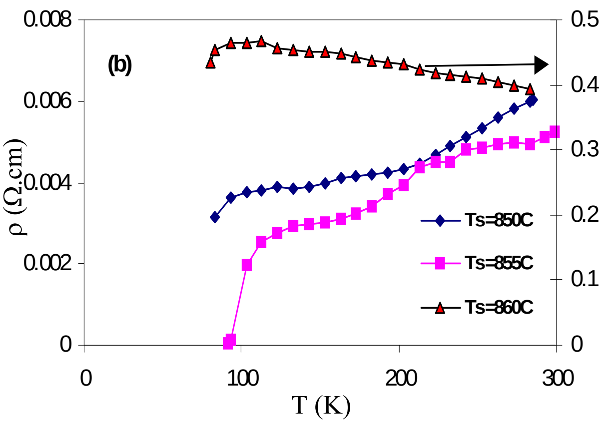


Fig. (4):Temperature dependence of resistivity for $(Bi_{0.8}Pb_{0.2})_2(Sr_{0.7}Ba_{0.3})_2Ca_2Cu_3O_{10+\delta}$ sintered at different temperature for 240 h in air.

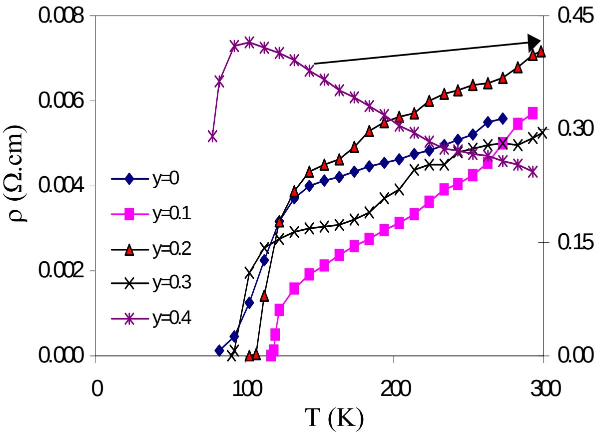


Fig. (5): Temperature dependence of resistivity for $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$

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 superconductors by producing $BaBiO_3$ and $BaCuO_2$ accompanied by high-T_C phase formation as referred by Kawai et al (14). 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 the highT_c phase.Enhancement of Ba to 0.4 will raise the resistivity and the behavior of the composition is converted to semiconductors. This may be due to the increase of formation of $BaBiO_3$ which is an insulator consisting of Bi (III) and Bi(V) (18).

The oxygen content (δ) of the samples were determined by iodometric titration, the values of (δ) were listed in table (1). It can be observed from figure(6) that T_C increase with the increasing of (δ) . This may be attributed to the presence of excess oxygen atoms in the Cu-O_2 layers and these atoms will create more holes in the perovskite layers, the creation of holes inCuO_2 sheet will shorten the Cu-O bond length and this will improve the transition temperature. Similar behavior of δ which the transition temperature was shown from Zhao et al (19).

It is interesting to note from table (1)and figure (7) that the oxygen content of the specimens gradually decrease as the sintering time is increased. During sintering, inorganic oxide present in the pellets gradually from $(Bi_{0.8}Pb_{0.2})_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ superconductor through various binary and ternary oxides phases. Some of them are

$Ca(BiO_2)_2$, $Sr(BiO_3)_2$, $CaPbO_3$and $SrPbO_3$. All these oxides have high oxygen content due to the presence of $Bi^V$and Pb^{IV} compounds. Therefore, initially these oxides present impurities in the high -T_c phjase and show a high oxygen content. As the time for sintering increases these impurities gradually convert to the high-T_c phase, which results in a gradual decrease in oxygen content.

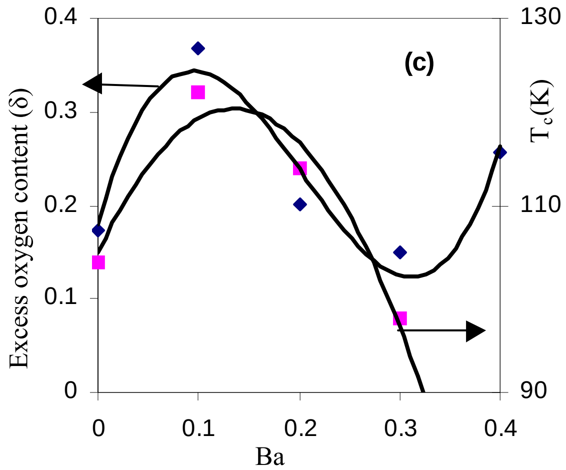


Fig. (6): Excess oxygen content (δ),transition temperature (T_c) as a function of Ba content

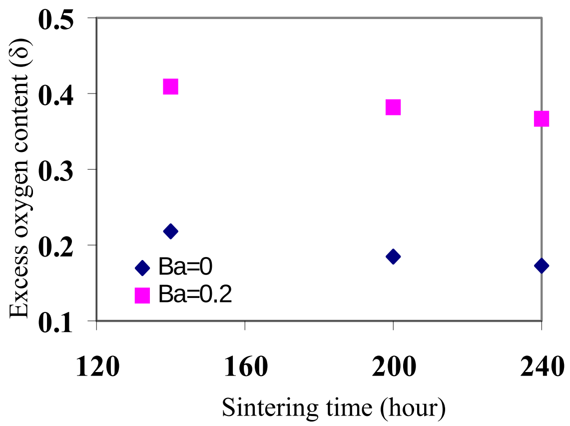


Fig. (7): Excess oxygen content (δ) as a function of sintering time

X-ray diffraction patterns for the Ba-free samples and the samples with different Ba contents with the Miller indices of orthorhombic structure, the full details of these work could be seen elsewhere ref.(20)are shown in figure(8). Two main phases were there in all the samples, i-e, high-$T_c$phase(2223), low-$T_c$phase(2212) and in addition a small amount of impurity phases, the appearance of more than two phases could be related to the stacking faults along the c-axis. The x-ray diffraction pattern for the Ba-doped samples exhibited a decrease of the low-Tc phase and an increase of the peaks of the high-Tc phase, and peaks corresponding to Ba compounds for example, $BaBiO_3$($2\theta=29^o$) and $BaCuO_2$($2\theta=29.3^o$ and 30^o) were strongly observed.

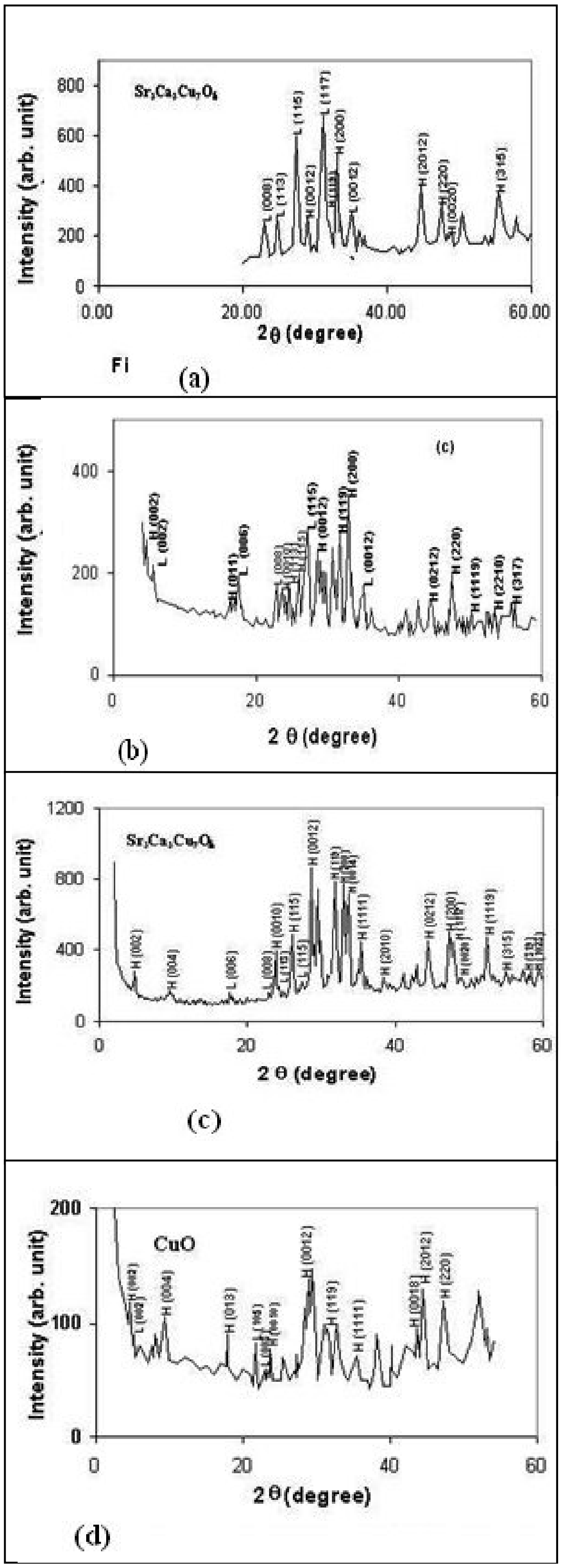


Fig (8) X-ray diffraction patterns for the sample with (a) y=0, (b) y=0.1, (c) y=0.2,and (d) y=0.3.

It is interesting to note that the cell volume increases with increasing y values, as shown in figure (9). This may be due to the substitution of Ba for Sr (depending on the ionic radii of Sr^{+2}(1.13 °A) and Ba^{+2}(1.35 °A).

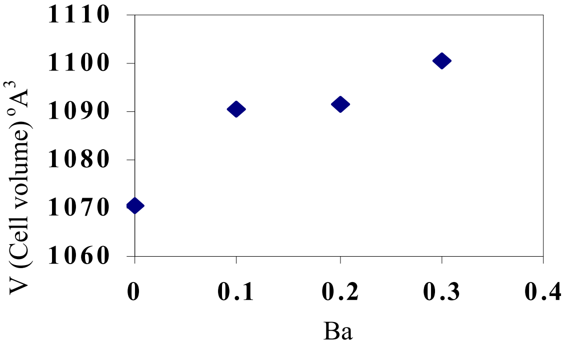
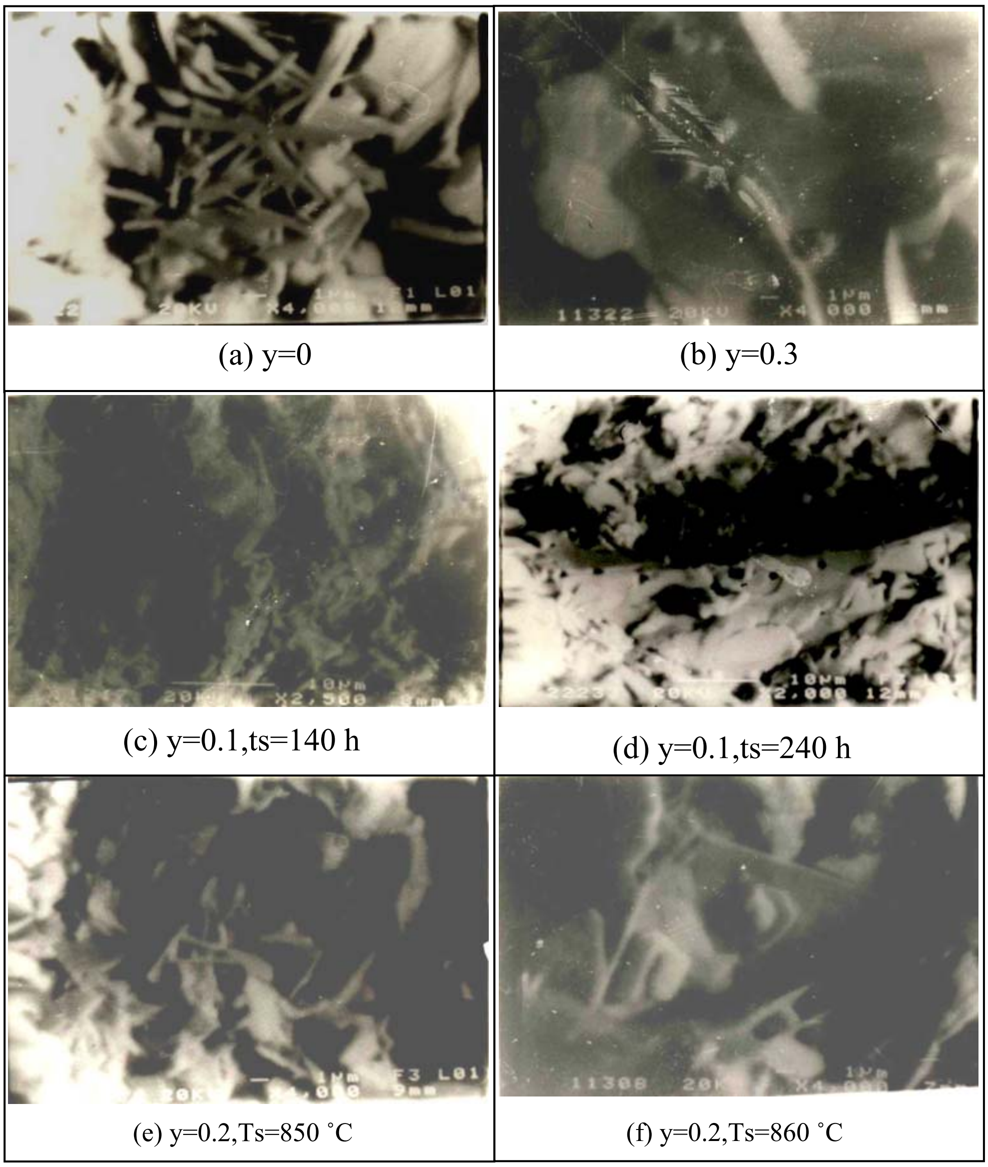


Fig. (9) Volume cell as a function of Ba content.

The scaning electron microscopy of fractured surface for the samples are shown in figure (10a-f). This figure shows the formation of two phases and thin elongated grains with no preferred orientation characterize microstructures. Among these particles there were some inclusions these are formed by a mixture of $CaCuO_3$ and CuO as indicated by Primo et al (21) together with the Ba content that are used in our samples.

The effect of sintering time for the sample with Ba=0.1 and sintering temperature for the sample with Ba=0.2 are shown in figure (10d,10f) respectively. It is found that a shape like pyramid could be formed from the accumulation of folds in figure (10d) while from figure (10f) it is found an ordinate geometrical shape (plate-like crystals) is belong to the high T_c phase.



(a) y=0 | (b) y=0.3 | (c) y=0.1,ts=140 h | (d) y=0.1,ts=240 h | (e) y=0.2,Ts=850 °C | (f) y=0.2,Ts=860 °C

Fig.(10): SEM photographs of fracture surface

Table (1) Values of (δ) and T_c at different sintering time

Ba	T_s(h)	T_c(K)	δ	Ba	T_c(K)	δ
0	140	94	0.219	0.2	100	0.41
	200	98	0.186		118	0.382
	240	104	0.173		122	0.368

Table (2) Values of (δ) T_c and volume cell for different compositions of $(Bi_{0.8}Pb_{0.2})_2$ $(Sr_{1-y}$ $Ba_y)_2Ca_2Cu_3O_{10+\delta}$

Ba	δ	T_c(K)	V (Cell volume) °A^3
0	0.17	104	1070.75
0.1	0.37	122	1090.51
0.2	0.20	114	1091.27
0.3	0.15	98	1100.60

Conclusion

Prolonged sintering time and divided the sintering processes are very important to obtain high T_c-phase. It is found that the optimum sintering temperature seems to be close to the partial melting point .The addition of Ba lowered the partial melting temperature for the $(Bi_{0.8}Pb_{0.2})_2$ $(Sr_{1-y}$ $Ba_y)_2Ca_2Cu_3O_{10+\delta}$ for y= (0-0.4).

References

1. Bednorz J. G. and Muller K. A. **1986**.Z. Phys. B, V. 64, P. 189.
2. Wu M. K., Ashburn J. R., Torng C. J., Hor P. H., Meng R. L., Gao L., Huang Z. J., Wang Y. Q. and Chu C. W. **1987**.Phys. Rev. Lett.,V. 58, P. 908.
3. Michel C., Hervieu M., Borel M. M., Grondin A., Deslandes F., Provost J. and Raveau B.: , **1987**.*"Superconductivity in the Bi-Sr-Cu-O System"* Z. Phys. B, V. 68, P. 421.
4. Maeda H., Tanaka Y., Fukutomi M. and Asano T., **1988**.*"A new High-T_c Oxide superconductor without a Rare earth element "* Jap. J. Appl. Phys., V. 27, No. 2, P. L 209.
5. Heh T. S., Chen J. R. and Tseng T. Y. **1990**. *"Preparation of $Bi_{0.7}Pb_{0.3}Sr_{1.0}Ca_{1.0}Cu_{1.8}O_y$High-$T_c$ superconductor by the Citrate method"* Jap. J. Appl. Phys., V. 29, No. 4, P. 652..
6. Huong P. V., Lacour C. and Hamdi M. M. **1993** *"Structure and Raman spectrum of $BiSr_2CaCu_2O_7$ (Bi_{1212}) superconductor"* J. Alloys and Compds., V. 195, P. 691.
7. Hong Z., Wang M., Xiong G. and Fan X. **1997**.*"Effect of Sr and Ca solid –solution behaviour on superconductive properties as determined by microstructure analysis "*Physica C, V. 288, P. 82.
8. Sumiyama A., Yoshitomi T., Endo H., Tsuchiya J., Kijima N., Mizuno M. and Oguri Y. **1988**.*"Superconductivity of $Bi_{0.25-y}Sr_{0.25}Ca_{2y}Cu_{0.5}O_x$(y=0.1,0.125,0.15)"* Jap. J. Appl. Phys., V. 27, No. 4, P. L542.,
9. Endo U., Koyama S. and Kawai T. **1988**.*"Preparation of the High –T_c phase of Bi-Sr-Ca-Cu-O superconductor"* Jap. J. Appl. Phys., V. 27, No. 8, P. L1476.
10. Takano M., Takada J., Oda K., Kitaguchi H., Miura Y., Ikeda Y., Tomii Y. and Mazaki H. **1988**.*"High-T_c phase promoted and stabilized in the Bi,Pb-Sr-Ca-Cu-O system"*Jap. J. Appl. Phys., V. 27, No. 6, P. L1041.
11. Mizuno M., Endo H., Tsuchiya J., Kijima N., Sumiyama A. and Oguri Y. **1988**.*"Superconductivity of $Bi_2Sr_2Ca_2Cu_3$ Pb_x O_y(x=0.2,0.4,0.4,0.6)"* Jap. J. Appl. Phys., V. 27, No. 7, P. L1225.
12. Ono A. **1988**.*"Crystallization of 107K Superconducting phase and partial melting in the Bi-(Pb)-Sr-Ca-Cu-O "* Jap. J. Appl. Phys., V. 27, No. 12, P. L2276.
13. Feng Q., Zhang H., Feng S., Zhu X., Wu K., Liu Z. and Xue L. **1991**.*"The process of forming 2223 phase from 2212 phase in Bi(Pb)-Sr-Ca-Cu-O system"* Solid state comm., V. 78, No. 7, P. 609.
14. Kawai T., Kawai S., Tanaka S., Horiuchi T., Takagi S., Ogura K., Kambe S. and Kawai M.: **1988**. *"Effect of Ba addition on the properties of Bi-Pb-Sr-Ca-Cu-O superconductors"* Jap. J. Appl. Phys., V. 27, No. 12, P. L2296.
15. Halim S. A., Mohamed S. B., Azhan H., Khawaldeh S. A. and Sidek H. A. A.: **1999**.Physica C, V. 312, P. 78.
16. Komatsu T., Ueta M., Ohki T., Sato R. and Matusita K. **1992**. J.Am.Ceram.Soc.75, 1864
17. Bunescu M. C., Aldica G., Badica P., Vasiliu F., Nita P. and Madache S. **1997**.*"SEM studies on BSCCO superconducting ceramic produced by spray frozen,freeze drying technique"* Physica C. V. 281, P. 191.

18. Manivannan V., Gopalakrishnan J. and Rao C. N. R. **1994**. J. Solid state chem., V. 109, P. 205.
19. Zhao J., Wu M., Abdul – Razzaq W. and Seehra M. S. **1990**.*”Interrelationship between the transition temperature of the 2223 and 2212 phases of Bi-based superconductores”* Physica C, V. 165, P. 135.
20. Hermiz G.Y., **2001**. *“Thermal Analysis and Phase Transformation of HTSc of* $(Bi_{1-x}Pb_x)_2(Sr_{1-y}Ba_y)_2Ca_2Cu_3O_{10+\delta}$ *Compound ”*, Ph. D. Thesis, Baghdad University, College of Science.
21. Primo V., Sapina F., Sanchis M. J., Ibanez R., Beltran A. and Beltran D. **1992**. Mater. Lett., V. 15, P. 149.