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Effect of Mn Substitution on the Superconducting Properties of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$

Ghazala Y. Hermiz, Bushra A. Aljurani, Md. Ali H. Al-Beayaty

Abstract*—The present study includes the preparation of Bi1.7Pb0.3Sr2Ca2-xMnxCu3O10+δ compound with x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 by solid state reaction method. The effect of the substitution of Mn on Ca site on superconducting properties has been investigated to obtain the optimum conditions for the formation and stabilization of the high Tc phase. Energy dispersive X-ray spectroscopy (EDX) analysis was used to test the proportions and energies of the elements of the compound. The crystal structure was examined by XRD for all superconductor samples; it was found that the crystal structure was orthorhombic and all major peaks in the spectra could be pointed to 2223-phase with amount of 2212-phase ; a small volume fraction of impurities like Ca2CuO3, CuO and Sr2Ca2Cu7Oδ were noticed in some samples. The highest Tc obtained for Bi1.7Pb0.3Sr2Ca2-xMnxCu3O10+δ composition was 118K for the sample with x=0.3.Scanning electron microscopy (SEM) has been used to identify the morphology of the superconducting phase and to investigate the influence of substitution effect of Mn on Ca site .The microstructure shows plate –like layered with increasing of voids and defect for samples with x=0.1,0.2,while the grains become smaller with disappear of grain boundaries of sample with x=0.3.

***Key Words*— Bi-based superconductors ,Mn substitution, · Scanning electronic microscopy.**

I. INTRODUCTION

Soon after discovery of high –T_c superconductivity in oxides in 1986 [1], worldwide efforts led to the development of oxides exhibiting superconductivity at temperature above the boiling point of liquid nitrogen [2,3] . Among the various Bi–Sr–Ca–Cu–O (BSCCO) system of high temperature superconductors (HTSCs) with the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$, the double-layered perovskite cuprates $Bi_2Sr_2CaCu_2O_8$ (n = 2) is of both fundamentals and technological interest since it has higher T_c and is amenable for the processing of the long length conductors and bulk devices[4,5]. Yildirim.et al. [6] studied the effect of Mn addition on the structural and superconducting properties of $Bi_{1.8}Pb_{0.4}Sr_2Mn_xCa_{2.2}Cu_3O_y$, ceramics with x=0,0.03,0.06,0.15,0.3 and 0.6 by means of XRD. They found that T_c values decreases from 109K to 85K : likewise, J_c reduce from 3200 A/cm² to 125 A/cm² with increasing Mn addition.

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According to the refinement of cell parameters done by considering the structural modulation, the Mn addition is confirmed by both an increase of the lattice parameter *a* and decrease of the cell parameter *c* of the samples in comparison with that of the pure sample (MnO) .From the SEM analyses they found that the surface morphology and the grain connectivity are degrade and grain size of the sample decrease with increase Mn addition.

Verma et al. [7] studied the effects of Mn substitution on the physical properties and structural properties of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Cu_3Mn_xO_y$for (x = 0.00, 0.10, 0.15 &0.20) . They found that the effects of Mn substitution favor the formation of Bi-2223 phases. the X-ray diffractometer reveals that all the samples crystallize in orthorhombic structure with lattice parameters (a = 5.4918 Å, b = 5.4071 Å, and c = 37.0608 Å) up to Mn concentration of x = 0.20.They found from the surface morphology that voids and grains size increases as the Mn concentration increased the nanosphere like structures on the surface of the Mn doped .

The surface morphology of $(Bi,Pb)_2Sr_2Ca_2Cu_{3-x}Mn_xO_{10+\delta}$ for ($0 \le x \le 0.3$) was studied by Kumar et al [8]:They found that the voids and grain sizes increase as the Mn concentration increases, and a nanosphere-like structures occur on the surface of the Mn-doped Bi-2223 sample. For x = 0, compact granular structures of variously shaped thin grains and larger pores are observed in some local region. In AFM view of the same surface the formation of the humps and roughness in some places can also be clearly seen, which is due to the formation of an oxide layer with different thicknesses, depending on the chemical composition of the phases.

Hawa et al. [9] studied the effect of Eu substitution onto Ca site in Bi(Pb)-2223 superconductor via co-precipitation Method, The critical current density (J_c) and superconductivity transition temperature $T_c(0)$ of Eu substituted were found to be lower than those of the pure sample. The crystallographic structure was found to change slightly from tetragonal to orthorhombic in Eu substituted samples. The lattice parameter c of the Eu samples decreased due to the incorporation of Eu^{+3} (0.95 Å) with smaller ionic size at the Ca^{+2} (0.99 Å) site. From the SEM investigation, the grain connectivity became weak and the porosity increased with the increment of Eu concentration, resulting in the decrease of J_c.

The aim of this work is to detect the effect of Mn content on the critical temperature (T_c), structure properties and microstructure of the (BPSCCO) compounds.

II. EXPERIMANTAL WORK

The samples of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$ for x=0,0.1,0.2,0.3,0.4, and 0.5 were prepared by a solid state reaction method ,using appropriate weights of highly pure materials Bi_2O_3,Pb_3O_4,$Sr(NO_3)_2$,CaO,MnO and CuO powders. The powders were mixed in the different stoichiomtric ratios and ground using agate mortar, a sufficient quantity of high purity 2-prorpanel was used to homogenize the mixture and to form slurry during the process of grinding for about 1h.Themixture put in the alumina crucible drying at 800^0C for 24h in a tube furnace in the air to remove CO_2, NO_2 gases from the mixture with rate (5˚C /min), then cooled to room temperature by the same rate of heating. The mixture then was pressed into disks shaped pellets of 13 mm in diameter and thickness of the pellet about (1.5-2) mm under pressure 0.7GPa.Then the pellets were put in an alumina crucible for sintering in the furnace at temperature of 830^0C for time 140h, then the samples were remove from the furnace and cooled to room temperature by the same rate of heating. Energy dispersive X-ray spectroscopy (EDX) type JEOL-SEM model jsm-7800F was used to analysis the compositions To study the effect of the Mn substitution at Ca site on the properties of Bi-based BSCCO, superconductor samples were characterized by X-ray diffraction (XRD), scanning electron microscopy(SEM), resistivity–temperature (R–T) measurements. SEM (type Evo 50microscope.) imaging was used to examine the surface morphology and grain structure of the samples

III. RESULT AND DISCSSIONS

To analysis the composition of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.9}Mn_{0.1}Cu_3O_{10+\delta}$ and $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.5}Mn_{0.5}Cu_3O_{10+\delta}$ bulk sample, energy dispersive X-ray spectroscopy (EDX) was used. The spectrum illustrated in Figs.(1&2) shows the elemental distribution in the sample. The results demonstrated that there is no unwanted element in the sample. This implies that the samples are not contaminated during the synthesis process.

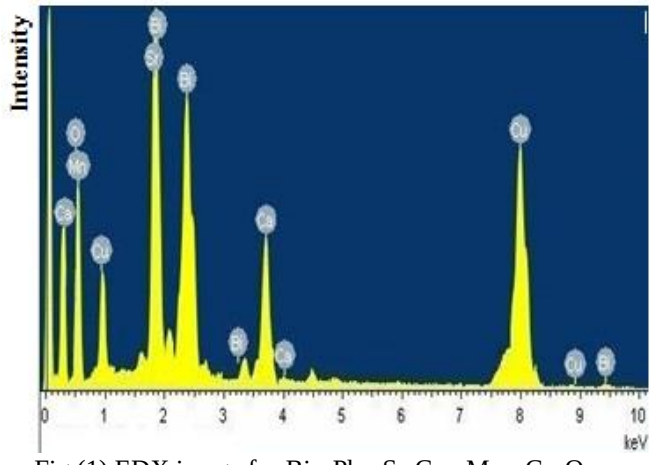

Fig (1) EDX image for $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.9}Mn_{0.1}Cu_3O_{10+\delta}$ composition.

In comparison between the two samples, substitution of Mn on Ca site was observed. Beside of the Mn peaks at 0.6 keV another peaks that belongs to Mn were appears at 5.9 and 6.5 keV for$Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.5}Mn_{0.5}Cu_3O_{10+\delta}$. On the other side there is a reduction of Ca intensity peaks. Other elements in samples such as Sr and Cu were not affected and the peaks still without any changed, this is an excellent proof that their preparation work is successful.

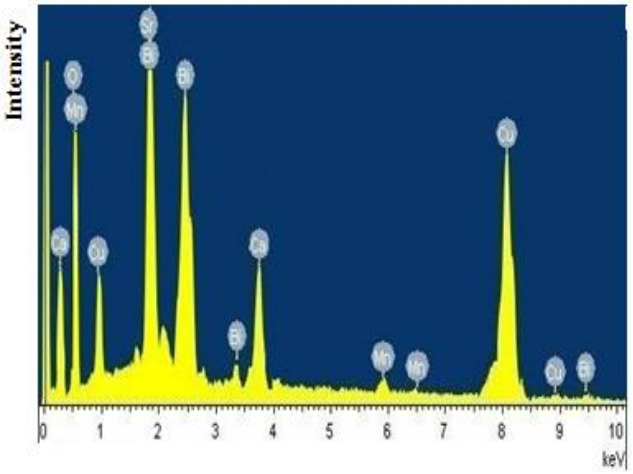

Fig (2)EDX image for $Bi_{1.7}Pb_{0.3}Sr_2Ca_{1.5}Mn_{0.5}Cu_3O_{10+\delta}$ composition.

A typical XRD pattern for the samples $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$ for different values of **x** prepared by solid state reaction Figs(3) indicating the dominant phase of Bi-2223 together with amount of low-phase Bi2212 with some impurity phase like Ca_2CuO_3, CuO and $Sr_2Ca_2Cu_7O_8$are detected at $2\theta \approx 32$, 35.25 and 36.8respectively [10].

It should be mentioned that the relative intensity of diffraction peaks varies slightly from samples prepared with different x. Fig (3)shows an increasing of the intensities for all peaks up to x=0.3, and these peaks are lowered with increase of Mn concentration. On the other side a present of H(0012) at 2θ=28.8 for all concentration of Mn is very important to prove the superconductivity for Bi-compound. Another peaks H(0018),H(200), H(2012),H(220),L(115), L(0012)and L(117)was found for all concentration of Mn. It also notes appearance of unknownpeakat 2θ=27º for x=0.1and 0.2 and disappear at another concentrations of x.

In addition, some peak intensities of the doped samples such as H (0012), L(117), L(0012), L(115), L(008) and H(117) increase regularly from x=0 to 0.3and then decrease to the x=0.5 , whereas the other peaks such as L(114), L(113) disappear completely as Mn substitution increases. On the other hand, L(0012), H (0018), H(2012), H(2014), H(1117) and H(220) peaks shifting to greater angles reach their top points at x = 0.5,while H (200), L(115), H (008) peaks shifting to lower angles reach their top points at x = 0.5.

Table (1) shows a reduction of the a and c lattice parameters for Mn-doped samples as comparable with the Mn- free samples ,It is well known that the lattice parameter *a* is controlled by the length of in-plane Cu-O bond [3].The length may be expanded or contracted with the change of the electrons into anti bonding orbital. On the other side the ionic radius of Mn (r_{Mn}=139±5 pm) is smaller than the ionic radius of Ca(r_{Ca}=176±10pm) thus the volume of the unit cell for manganese doped sample is smaller than the undoped sample. Indeed the behavior of the lattice constant may attribute to the displacement of Mn ions instead of the Ca ions.

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The variations of lattice parameters indicate the intercalation of oxygen species. This change of a, b, c effect on the volume of the unit cell and then causes variation of the density.

The ratio c/a for all the prepared samples has also been calculated as shown in Table (1).

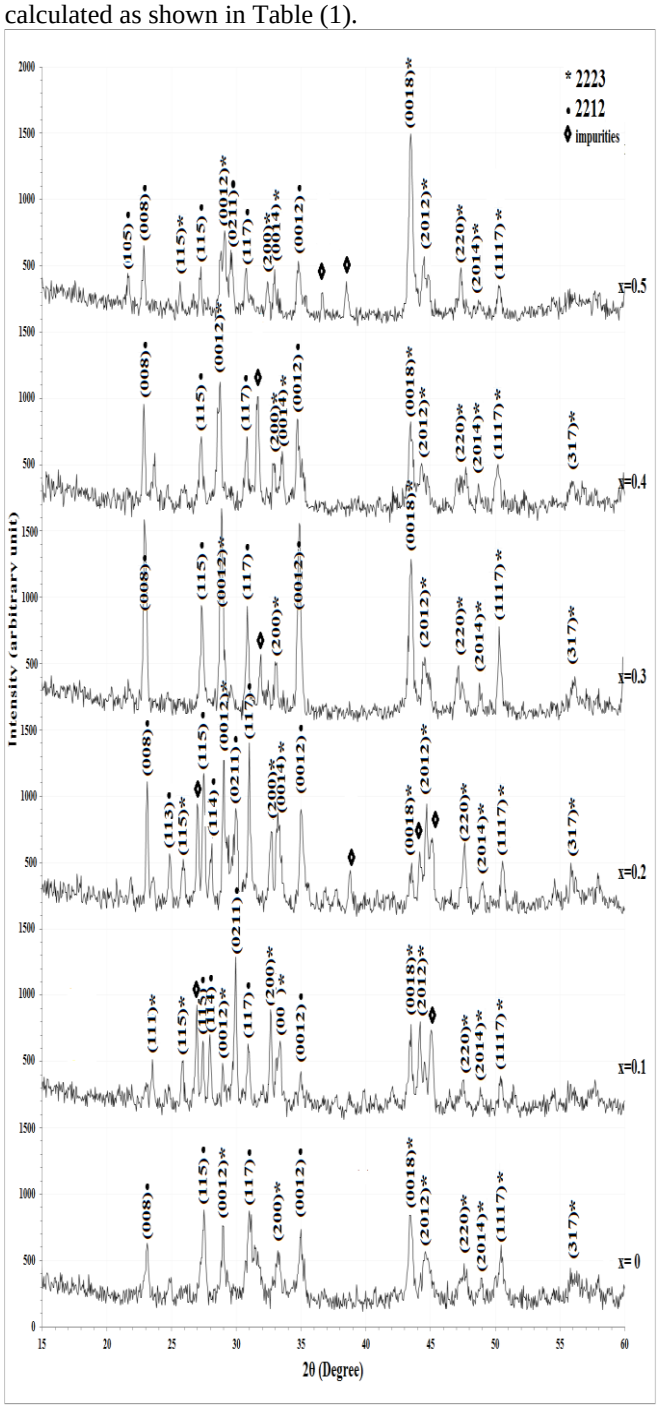

Fig (3) X-ray diffraction patterns of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$ for different nominal composition.

The effect of Mn substitution in Ca site on electrical resistivity has been investigated .It is found that most samples show a metallic behavior above the T_c. Moreover, the zero-resistivity transition temperatures (R = 0) deduced from the dc resistivity measurements.

The variation of dc electrical resistivity measured with temperature by the standard four probe technique for the $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$ samples, with (x=0, 0.1, 0.2, 0.3, 0.4 and 0.5) are shown in Fig (4). All the curves exhibit a transition from normal to the superconducting state .The critical transition temperature T_c are determined from this figure are shown in Table (1).It is It is found that T_c value increase with increasing of Mn substitution up to 0.3. This increasing is related to the increase of the relative percentage of (Bi, Pb)-2223 phase formation. Besides, the broadening of the resistive transition increases as the Mn content enhances except x=0.5, confirming the presence of impurities (as shown in XRD results) and weak links between the superconducting grains. Fig.(5) shows the critical temperature versus Mn content for the samples. It is found from above results that the concentration of Mn up x=0.3 could be improve the behavior of superconductor and the transition temperature of stoichiometric composition.

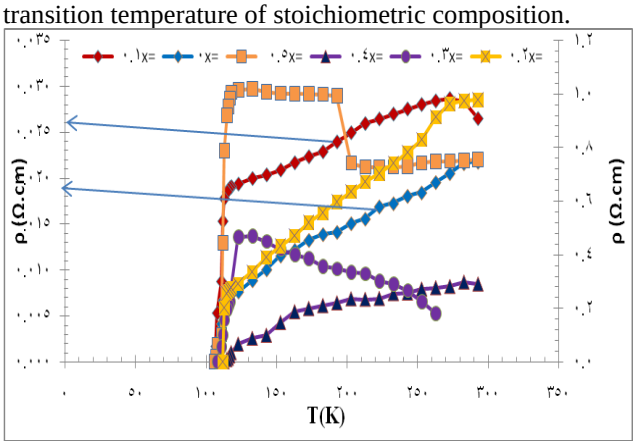

Fig (4): Temperature dependence of resistivity of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$ for different nominal composition.

Table (1) : lattice parameters, c/a , volume of unit cell (V) and transition temperature for different composition of $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$.

x	a(Å)	b(Å)	c(Å)	c/a	V(Å)^3	T_c(K)
0	5.4324	5.4314	37.6109	6.9234	1109.74	105
0.1	5.4215	4.9760	37.1826	6.8583	1003.08	107
0.2	5.4051	5.3497	36.8619	6.8197	1065.90	110
0.3	5.4260	5.4309	37.5259	6.9159	1105.83	118
0.4	5.3848	5.1733	37.4375	6.9523	1042.92	115
0.5	5.3855	5.4241	36.5022	6.7778	1066.29	114

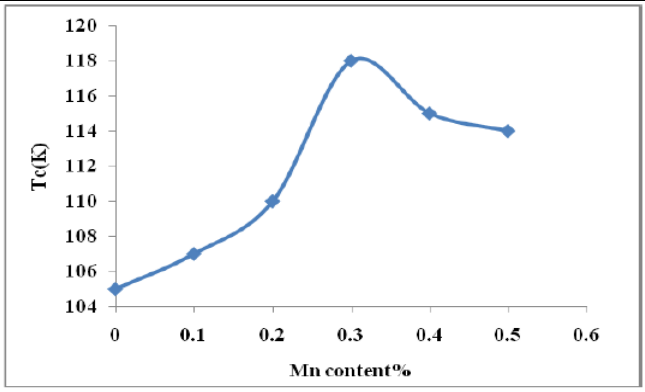

Fig.(5) T_c as a function of Mn content for $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$ samples.

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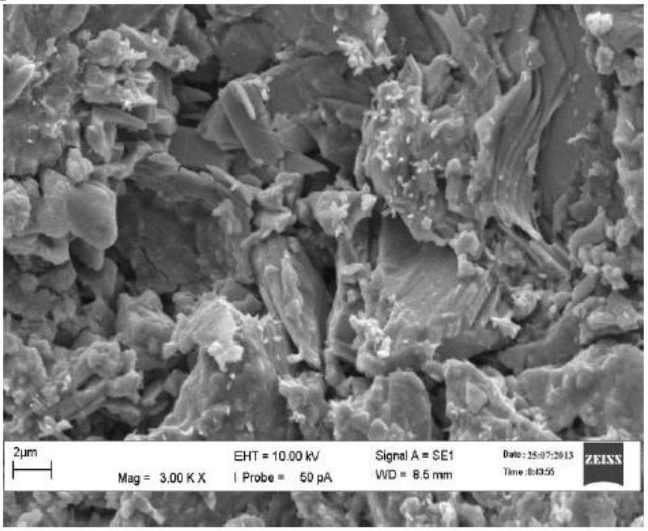
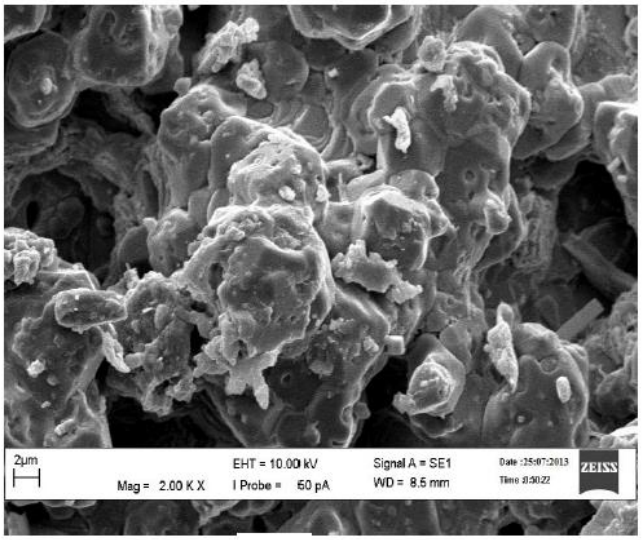
The grain structures can be easily examined by the SEM micrograph. In the samples, all of the grains headed randomly and grain boundaries seem to be in touch with each other as to make weak bonds. Also, this is one of the most characteristic properties of the high-temperature superconductors The SEM images of the surfaces of as synthesizedsamples- are shown in Figs.(6a-f). In the undoped sample, a homogeneous and layered structure was formed. In sample x=0.1 there are more number of voids and homogeneity was a little bit deformed in comparison with sample free of Mn. Also, the alignment of plate-like structures changed in sample x=0.2. In sample with x=0.3, layered structures have been alignment and grains become smaller with disappear the grain boundaries. Indeed grain boundaries inside the microstructure of the samples act as the barrier to scatter the conduction of carriers, the decreasing of the number of grain boundaries leading to the reduction of this insulating region and thus enhanced the grain connectivity [11]. Among the plate-like structure there were some inclusions these could be due to the Mn content that used in our samples, or to the formation of Ca_2CuO_3as indicated by Primo et al [12].A crack which is due to either increased Mn concentration or increased the temperature at near melting point was found for sample with x=0.4. The presence of MnO2 influenced the average size of 2223 phase.



(a)



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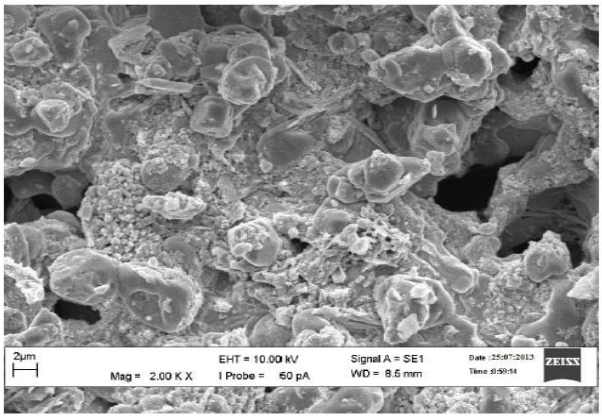

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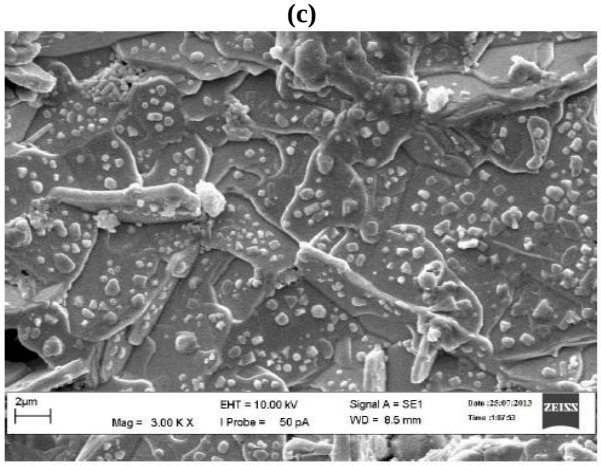
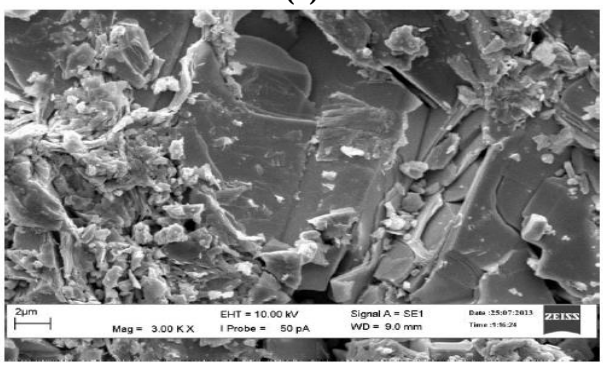
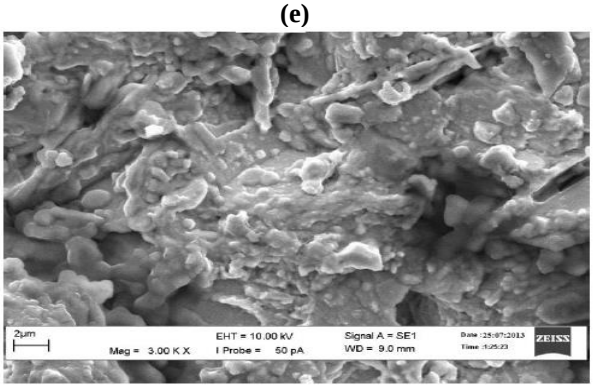


(d)



(e)



(f)

Fig(6)Scanning electron microscopy (SEM) images of the Mn substituted sample (a)x=0.0 (b) x=0.1(c)x=0.2 (d) x=0.3(e)x=0.4 and (f) x=0.5

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IV. CONCLUSION

It has been noticed that the substitution of a certain value of Mn content on the Ca site in $Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x-}Mn_xCu_3O_{10+\delta}$ plays a great role in producing good superconducting samples.

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