ENHANCEMENT OF T_C BY SUBSTITUTION OF (Pb AND Nd) IN BISMUTH-BASED HIGH- T_C SUPERCONDUCTORS MATERIAL

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Bulk polycrystalline samples with a nominal composition $Bi_{2-x}(Pb,Nd)_xSr_2Ca_2Cu_3O_{10+\delta}$ for (x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6) have been prepared by solid state reaction method. The effect of the partial substitution of (pb,Nd) for Bi on superconducting properties has been investigated. Eelectrical resistivity measurements showed that the doping of Pb and Nd enhance transition temperature and produced superconductor samples, in which the higher T_c value was 118K found for the composition x=0.2. On the other hand X-ray diffraction (XRD) analysis showed an orthorhombic structure with a high T_c phases (2223) as a dominant phase. The surface area images of some specimen show the particles appear with different shapes (spherical grains, needle- like grains and irregular grains).

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1. Introduction

Since the discovery of a High T_c superconducting phase in the Bi-Sr-Ca-Cu-O (BSCCO) system by Maeda and his coworkers in January 1988 [1], extensive research has gone into the areas of processing, characterization, phase equilibria, physical property measurement, and device fabrication of these materials. The BSCCO compound consists of an oxygen deficient perovskite layer containing copper oxide planes sandwiched between bismuth oxide layers .The number of copper oxide planes corresponds to the n in the chemical formula $Bi_2Sr_2Ca_{(n-1)}Cu_nO_x$ where n = 1, 2, or 3. As the number of copper oxide planes increases, the critical temperature increase [31]. Bi-2223 has a tetragonal, layered, orthorhombic perovskite structure composed of two charge-reservoir layers (Bi-O, Sr-O) sandwiching three CuO_2 planes of strong superconductivity. The value of these parameters changes slightly depending on the cationic substitution. Partial substitution for Bi^{3+} by ions of various radii and valence such as Pb^{+2} in $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ compound may be effect HTSC phase formation, chemical stability and the superconducting properties [2].

The advancement of understanding the physics of superconductivity and appearance of applications depends strongly on the development in materials research that it is still in progress.

The superconducting properties controlled by the addition or substitution of an elements with different ionic radius and bonding characters; Therefore, Pb and Nd are the most important substituting element that influences the microstructure, phase composition, and the related superconducting properties of the BSCCO system.

2. Experimental

Starting materials of high- purity powders (99.9%). of (Bi_2O_3, Pb_3O_4, $Sr(NO_3)_2$, CaO,CuO and Nd_2O_3) were used to prepare the system $Bi_{2-x}(Pb,Nd)_xSr_2Ca_2Cu_3O_{10+s}$ with ($0 \leq x \leq 0.6$). Then pressed the mixture into pellets under pressures 0.7 GPa using hydraulic press type (Specac). The samples were sintered at 850° C for 160 hr.

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The most common method of determining the T_c of a superconductor is the resistivity measurement by using the four-point probe method in a cryostat with presence of liquid nitrogen. The crystal structures for the samples prepared from the compounds $Bi_{2-x}(Pb,Nd)_xSr_2Ca_2Cu_3O_{10+\delta}$ were obtained by (XRD) method, using X-ray diffractometer type Philips.

The iodometric titration was a simple chemical method used to determine the oxygen content in BSCCO samples [3] .Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) type FEI-SEM model Inspect-S50 were used to study the surface topography and analysis the composition of the samples.

3. Results and discussion

Energy dispersive x-ray pattern (EDX) was used to confirm Bi_2Sr_2 $Ca_2Cu_3O_{10+\delta}$ and $Bi_{1.8}(Pb_{0.1}$, $Nd_{0.1})Sr_2$ $Ca_2Cu_3O_{10+\delta}$ samples sintered at 850^0C for 160h. The spectrum illustrated in Figs. (1a,b) shows the element distribution in the sample. The results demonstrated that there is no unwanted element. This implies that the sample are not contaminated during the synthesis process.

All peaks show that there are no changes in the position of Bi, Sr, Ca and Cu peaks after the partial replacement of the Bi ions by Pb and Nd. These results indicate that these ions are well substituted in the microstructure of Bi-2223.

A substitution of Nd with Bi site was observed at 0.9KeVand 5.2 KeV,while pb was observed at 2.5 and 10.6kev for x= 0.2. On the other side there is a reduction of Bi,Sr,Ca,and Cu peaks for the sample $Bi_{1.8}(Pb_{0.1}$, $Nd_{0.1})Sr_2$ $Ca_2Cu_3O_{10+\delta}$. In addition it has been notes from Fig. (1b) that Pb ions have partially replaced Bi in the system.

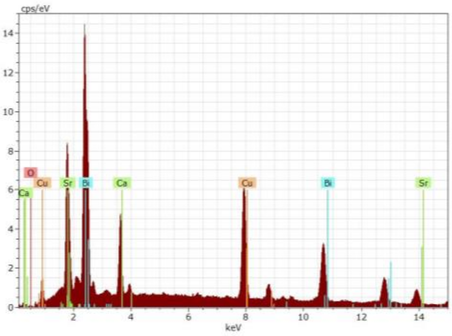

Fig. 1a .EDX image for $Bi_{2-x}(Pb,Nd)_xSr_2Ca_2Cu_3O_{10+\delta}$ composition sintered at 850 ^{o}C for x=0

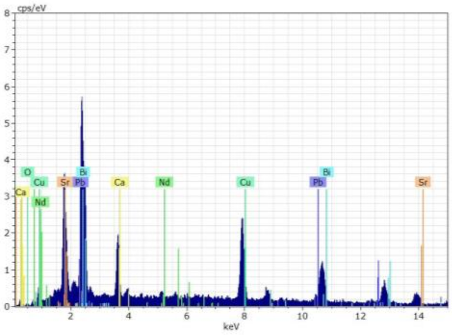

Fig. 1b. EDX image for $Bi_{2-x}(Pb,Nd)_xSr_2Ca_2Cu_3O_{10+\delta}$ composition sintered at 850 ^{o}C for x=0.2.

The resistivity versus temperature for samples with nominal composition $Bi_{2-x}(Pb, Nd)_xSr_2$ $Ca_2Cu_3O_{10+\delta}$ ($0\leq x \leq 0.6$) sintered at 850 ^{0}C are shown in Fig. (2).

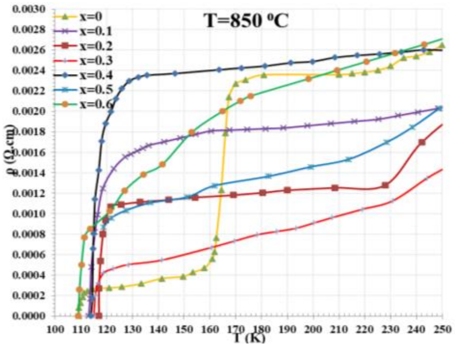

Fig. 2. Variation of electrical resistivity as a function of temperature for all samples sintered at T =850 ^{o}C.

It is found from this figure that the addition of 0.1 and 0.2 (pb, Nd) content to the composition will raise the transition temperature. (see Table 1)

While excessive (pb, Nd) addition ($x \geq 0.3$) promotes another reaction, which is likely to assist the formation of low- T_c phase and decrease the transition temperature similar results mentioned by Abbas et al. [59] .Such a decrease can be attributed to the rise of grain boundaries which act as poor contact within the 2223- phase.

To elucidate the structure changes accompanying with partial substitution of (pb, Nd) for Bi in Bi_2Sr_2 $Ca_2Cu_3O_{10+\delta}$ compound and to explore there possible relationship with critical temperature, the crystal structure of doped samples has been studied by the X-ray diffraction analysis.

The x-ray diffraction patterns of free and doped superconductor samples have been taken for $0 \leq x \leq 0.6$, the peak positions intensities of the diffraction data have revealed that our sample consists of the Bi-2223 phase and a small amount of Bi-2212 as a minor phase together with some other unidentified peaks. We have seen an improvement in the structure properties and the higher rate of phase Bi-2232 that appears at x=0.2. These XRD patterns showed in Figs. (3).

The intensity of some reflection lines such as H(111), H(0012) and H(1111) become less for the $x \geq 0.3$. This suggested increasing the dopant concentration which allows to from the low phases i.e by increasing the dopant concentration, the stability of Bi-2223 phase appears to be altered as indicated by Wang et al. [5].

This may be attributed to the substitution of (pb,Nd) case more cuprite vacancies that the HTSc need to a high scattering effect of supper electrons in crystalline structure [6].

It should be mentioned that the position of diffraction peaks varies slightly for sample prepared with different values of x, which is predicted from the change in lattice constant. These results are found to be in agreement with the resistivity measurement. Table (1) notice the variation of lattice parameters (a, b, and c) with substitution of (pb,Nd) for Bi.

For doped samples it is clear that c-lattice parameter increases with increasing of substitution (pb,Nd) from 0.1 to 0.2. Then there is reduction of c-lattice parameter with increasing of (pb, Nd) content, this behavior agreed with Aloysius et al. [7].

However the reason of the deformation c-axis as results of substitution is due to the difference in the ionic radii of Bi^{3+} (0.96A^{o}), Pb^{2+} (1.19 A^{o}), and Nd^{3+} (1.109 A^{o}) which renders c-parameter to be longer or get deformed [7].

The perfect perovskite structure of the studied systems have built in deformation comes firstly from the difference in the size of the atoms in the body centered part of the perovskite lattice structure, secondly from the vacant sites of the oxygen atoms [8]. Through the values a,b, the ratio c/a and the density (ρ) of the unit cell have been calculated as shown in the Table (1).

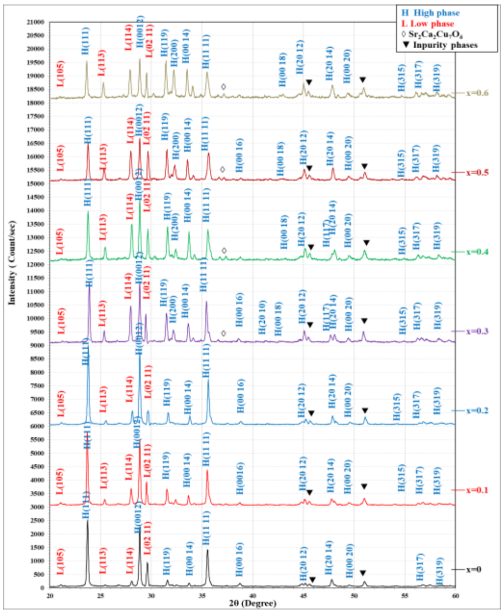

Fig. 3. XRD patterns of $Bi_{2-x}(Pb,Nd)_xSr_2Ca_2Cu_3O_{10+\delta}$ bulk samples for x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) sintered at 850 ^{0}C for 160h.

Most of the physical properties are very sensitive to the oxygen content in high-T_c superconductors. Therefore, it is important to report the oxygen content of the sample on which the physical measurements are made.

Idiometric titration method has been used to measure the excess of oxygen content (δ) for the samples $Bi_{2-x}(Pb,Nd)_xSr_2$ $Ca_2Cu_3O_{10+s}$ with ($0\leq x\leq 0.6$), the results are listed in Table (1) and plotted in Figs. (4).

It is interesting to note from these figures and Table that there is a direct relationship between oxygen content and transition temperature [9].

The T_c increase with increasing δ as the concentration of (pb,Nd) increases from x=0 to x=0.2. This could be assigned to the presence of excess oxygen atoms in the Cu-O_2 layers which create more holes in the perovskite layers, the formation of holes will shorten the Cu-O_2 bond length and this leads to an improvement of the T_C the optimum value of δ is at x=0.2 (this consist with results of resistivity).

Besides that, increasing the values of x up to 0.3 will be decreasing both δ and T_c.

This could be attributed to the increase of oxygen absorption during crystallization process of the superconductors [10].

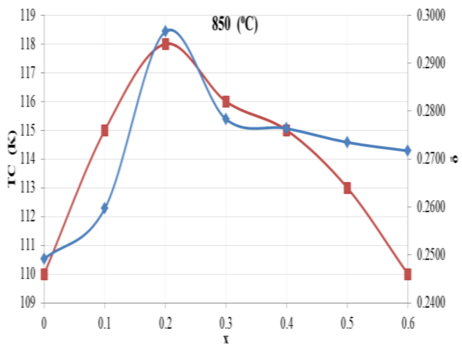

Fig. 4. Variation of the critical temperature T_c and oxygen content (δ) as a function of of x.

Table 1. Variation of values of lattice parameters, c/a, volume of unit cell V, volume fraction and density ρ_m for different composition of $Bi_{2-x}(Pb, Nd)_xSr_2\,Ca_2Cu_3O_{10+\delta}$.

X	T_c (K)	δ	a (Å)	b (Å)	c (Å)	V ($Å^3$)	c/a	ρ_m (g/cm^3)	V2223%	V2212%
0	110	0.2492	5.4069	5.2625	37.4709	1066.179	6.9302	1.5946	69.15	30.85
0.1	116	0.2597	5.4018	5.1868	37.4109	1048.197	6.9256	1.6167	72.08	27.92
0.2	118	0.2966	5.4017	5.1746	37.5953	1050.849	6.9599	1.6074	73.07	26.93
0.3	116	0.2783	5.4040	5.3692	37.2379	1080.446	6.8909	1.5582	69.88	30.12
0.4	116	0.2764	5.4255	5.2176	37.3372	1056.940	6.8818	1.5876	69.69	30.31
0.5	113	0.2735	5.4629	5.1039	37.4471	1044.092	6.8548	1.6019	66.88	33.12
0.6	114	0.2717	5.4453	5.1709	37.4365	1054.085	6.8751	1.5815	65.43	34.57

SEM micrographs of the fractured surfaces for the prepared samples are shown in Figs. (5). It obvious from these images that the samples consisting of packets of plat-like shape. Some of the plates have grown one through the other, in different directions, giving rise to bigger grains. The surface area images of some specimens show how the particles appear with different shapes (spherical grains, needle-like grains and irregular grains).

For pure sample the needle-like grains growing normally at the surface and some long plate-like grains growing out of the packet. Another important microstructural features are observed in Figs. (5b) and (5c) the texturing needle-like grains, clump of whisker, spherical grains, plate like structures and layered grain are less than that of pure sample, but the grain size is lager this may due to coalescence, T_c for these samples could be higher than the other samples. similar results where pointed out by Takano et al. [11].

For the samples that have x≥0.3 big grains seem to have decomposed into small grains, as the result that the samples have low T_c. From the above result, we can conclude that (pb, Nd) doping (x≤0.3) may primate the formation of high phase (2223) as well as improve the critical transition temperature.

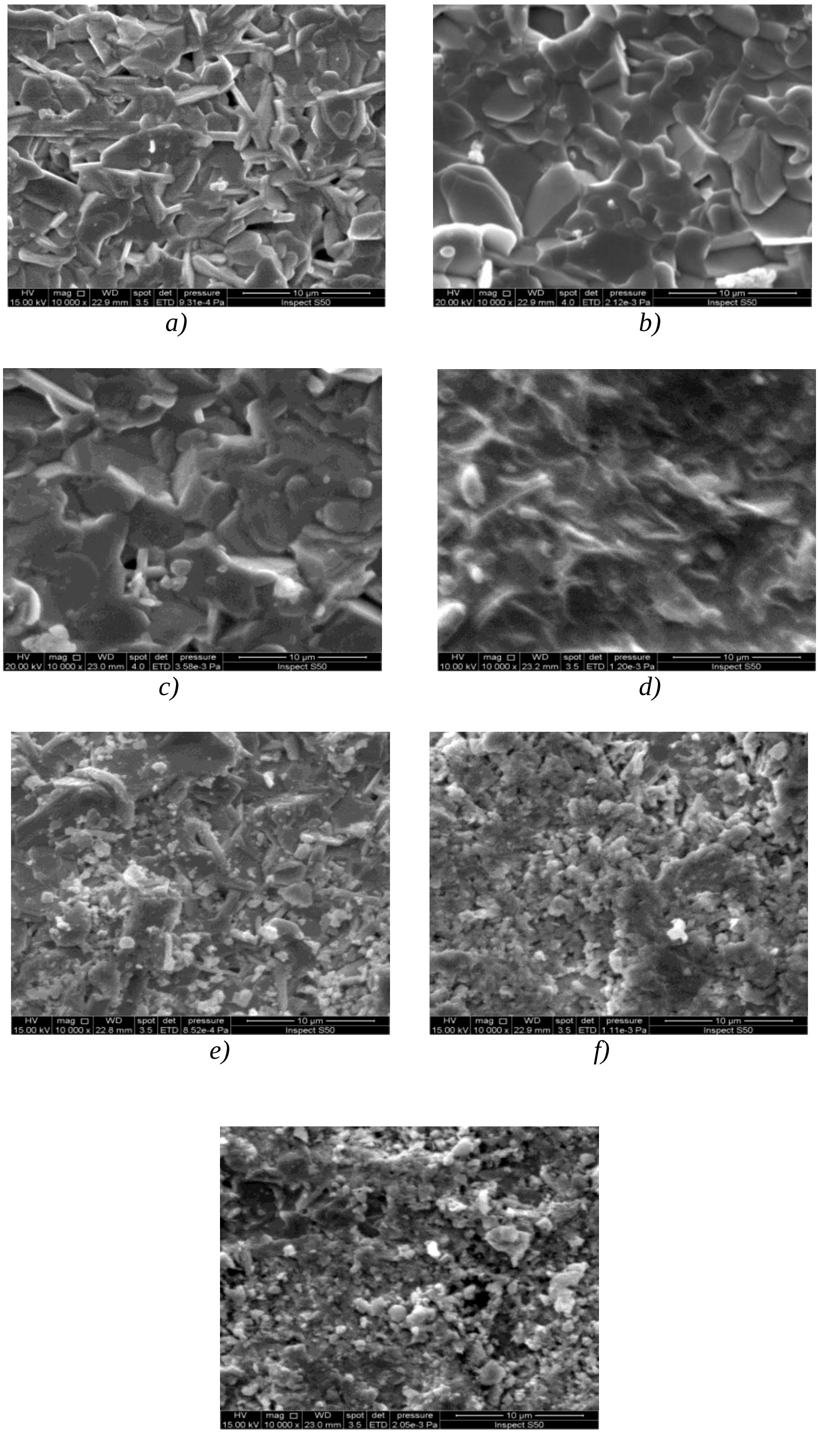

Fig. 5. SEM micrographs of fracture surface of $Bi_{2-x}(Pb, Nd)_xSr_2\ Ca_2Cu_3O_{10+\delta}$ sample with
a) x=0; b) x=0.1; c) x=0.2; d) x=0.3; e) x=0.4; f) x=0.5; g) x=0.6

4. Conclusions

$Bi_{2-x}(pb,Nd)_XSr_2Ca_2\ Cu_3O_{10+\delta}$ has successfully prepared using solid state reaction. Doping of Nd and pb in $Bi_{2-x}(pb,Nd)_XSr_2Ca_2Cu_3O_{10+\delta}$ has showed a maximum value of T_c= 118 K and optimum value of excess of oxygen content (δ=0.2966) for x=0.2 .

XRD results showed on orthorhombic crystal structure for all samples and there are two superconducting phases with exist of impurity phase.The microstructure of all samples which have been studied by (SEM) are characterized by needle-like grains with low porosity.

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