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Effect of Partial Substitution of Lanthanum (La) on the Structural and Electric Properties of $Bi_2Sr_2Ca_2Cu_{3-x}La_xO_{10+\delta}$

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Abstract

In the current study, we investigate the effect of (La) substitution instead of (Cu) on the properties of the superconductor compound ($Bi_2Sr_2Ca_2Cu_{3-x}La_xO_{10+\delta}$) with (x=0,0.05,0.1,0.15,0.2). The samples were prepared by solid state reaction method(SSR). X-ray diffraction technique (XRD) was used to estimate the structural properties of the specimens which show an orthorhombic crystalline structure for all the specimens.

The results show that the change in (La) concentration leads to decrease the concentration of (Bi-2223), increment in (Bi-2212) and(Bi-2201) with appearance of some impurities. Also decrease the critical temperature(Tc) with the increase of (La) concentration.

Key words : Lanthanum substitution, (Bi-2223) superconductor, structural properties, Critical temperature.

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Introduction

Many researches were interested in preparing structure and properties of the superconductive compound since the discovery of the high temperature superconductors for the system (Bi-Sr-Ca-Cu-O)(BSCCO)[1].

The Bi-based superconductive systems has layers structure so it consists of three phases including Bi-2201,Bi-2212 and Bi-2223[2].The last number of each phase means the number of layers of CuO which has the critical temperatures (10K,80Kand110K) consequently; the last means the temperature at which the electrical resistance equal to zero (R=0)[3].

It is difficult to prepare the phase (Bi-2223) which is characterized by the highest critical temperature (110K) among the three phases as a single phase. The properties of superconductors can be controlled by adding or substituting an element different in its ionic radius and its bonding features, the improvement or deterioration in the superconductors properties depends on the features of added or replaced elements that are different in their radius and bonding properties so most studies concentrate on the fashioning and properties improvement in (Bi-2223) depending on substitution studying[4]. The phase(Bi-2223) is considered the most important phase in the system(BSCCO) because it is characterized by high critical temperature and critical current intensity [5].Also it has a promising future in high magnetic field applications at liquid nitrogen temperature; generally the third phase form is ($Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$)[6].

The studies on Pb,Sb,Cd and Ag substitution instead of bismuth show that the addition of small amount of Pb improves the critical temperature from (92K to 106K) while the addition of Pb and Cd instead of bismuth leads to increase the transition temperature from (85K to 110K),also the partial substitution of(Ba) instead of(Sr),(Pb and Hg) instead of (Bi) leads to improvement of some ($Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$) properties. These substitutions improve (Bi-2223) formation, support and improve the superconductivity because they lead to a high critical temperature reaching (129Kand125K) for the compounds ($Bi_{1.75}Hg_{0.25}Sr_{1.9}Ba_{0.1}Ca_2Cu_3O_{10.271}$),($Bi_{1.75}Pb_{0.25}Sr_{1.9}Ba_{0.1}Ca_2Cu_3O_{10.26}$) consequently. Also the substitution of(Bi) by(Ag) leads to improvement in properties and increasing the critical temperature from (110Kto 129K).[7-11]

Other researchers study the partial substitution effect of (Li) and (Cd) instead of (Bi) in the superconductive compound($Bi_2Pb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$),the specimen prepared by solid state reaction and the (XRD) show that all specimens are orthorhombic crystalline structure and contain the phases (Bi-2212,Bi-2223) for both. The electrical resistivity measurement shows that the highest critical temperature values equal to (130K,126K) at substitution ratio (0.3,0.2) in(Li,Cd) usage respectively, with a noticeable increment of c/a in case of substitution by (Cd).[12,13]

Also studying the partial substitution of(Mn)and(Mg) instead of (Ca) on the properties of the superconductive compound ($Bi_{1.7}Pb_{0.3}Sr_2Ca_{2-x}Mn_xCu_3O_{10+\delta}$) and ($Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Mg_xCu_3O_{10+\delta}$) respectively ,both specimens prepared by solid state reaction,(XRD)show an orthorhombic crystalline structure and (Bi-2223) phase more than (Bi-2212) phase with the presence of very small amount of impurities for both. The measurement of electrical resistivity shows that the highest critical temperature value(T_c=118K) at(x=0.3) in case of substitution by (Mn),while in case of (Mg) substitution the highest critical temperature value(T_c=104K) at(x=0.2) and the c/a of the highest value.[14,15]

The properties of the superconductive system($Bi_2Sr_2Ca_2Cu_3O_x$) has been studied where the specimens prepared by solid state reaction method with different temperatures and sintering time and the results of(XRD)show that all specimens contain the phases(Bi-2201,Bi-2212,Bi-2223)and some other non superconducting phases($Sr_{8.5}Bi_6Ca_{2.5}O_{22}$),the crystalline structure of (Bi-2223) is orthorhombic ,and he conclude that the best and more successful way of preparation and formation of(Bi-2223) is the solid state reaction method.[16]

On the other hand (La) substitution instead of (Ca) leads to decrement of(Bi-2223) concentration, (Bi-2212) concentration increment, decreasing the critical temperature and transforming the superconductor compound to insulator behavior by increasing (La) content.[17]

The results of (Ni) substitution instead of (Cu) shows decreasing in Tc and changing of some compounds at certain concentration of(Ni) from superconductor to insulator with increasing Ni concentration[18].The study of (Cu) replacement by (Li) shows an orthorhombic crystalline structure for all the specimens and T_c increment with increasing (Li) concentration[19].The (XRD) in studying (Mg) substitution instead of (Cu) in (Bi-2223)at concentration(0-0.7) shows the presence of(Bi-2212) in the crystalline structure beside the presence of other phases of impurities while the electrical resistivity measurement shows a little effect on onset and offset transition temperature at (R=0).[20]

Other study reached to the results that (Cu) substitution by metallic ions leads to deterioration of superconductive properties and the degree of deterioration depends especially on the type of ion. Generally the greatest suppression in superconducting occurs when the ion occupy the (Cu) position in layers(Cu-O) while a less suppression occurs when the ion occupy the (Cu) position in the linear chain[21].In this work we succeeded in preparation of a polycrystalline superconductor compound **(**$Bi_2Sr_2Ca_2Cu_{3-x}La_xO_{10+\delta}$) as a pellets shaped specimens by using the solid-state reaction and we study the effect of (La) substitution instead of (Cu) on its electrical and structural properties.

Materials and methods

Preparation of samples by the solid-state reaction using a specific weight of highly purified oxides powder of (Bi_2O_3,SrO,CaO,CuO,La_2O_3).Calculations of the appropriate weight for each oxide. Drying specific amounts of powders in oven under (125℃) for (1.5hr) to get rid of humidity then reweighting by a highly sensitive digital balance (4-digit), mixing and grinding by an electrical vortex mixer for(6hr) to get the best state of homogeneity . After that the resulted powders were dried at (125℃) for (1.5 hr) and compressed by a hydraulic compressor under (7tons/cm^2) compression force for (1 minute) as pellets of (1.5 cm) diameter and (0.15-0.25 cm) thickness. Sintering at (750℃) for(140 hr) at heating rate (5℃/min) to get an interlinked material and to ensure a gradual diffusion as much as possible. The last step is cooling to room temperature at the same heating rate. Investigating the specimen by (XRD) to get the structural properties in a diffraction angle ranging from (10°-70°),estimation of the lattice parameters(a,b,c) using the d-value and (hkl) reflections mathematically depending on Braggs law of (XRD),then measure the unit cell density and calculate the formed phases concentrations according to the following equation:[17]

$V_{(phase)}=\sum\Gamma_a/\sum\Gamma_1+\Gamma_2+...........+\Gamma_n$---------------(1)

Γ_a =intensity value of the target phase peak,$\Gamma_1,\Gamma_2,...,\Gamma_n$ =intensity values of all peaks in XRD.

A four probe technique were used to measure the electrical resistivity as a temperature function with the aid of nanovoltemeter and constant current source, with cooling by the liquid nitrogen.

Result and discussion.

Figure (1). shows the (XRD) pattern for (Bi-2223) doped by (La),from diffraction positions and peaks,we see that all the specimens contain a high percentage of the high temperature phase (Bi-2223). A few peaks of low intensity phases (Bi-2212andBi-2201)that has a low temperature, with appearance of some impurity phases.

Figure (2).shows the comparison of (Bi-2223)in the pure specimen and in the (La) doped specimen , it was noticed that there are a decrement in this phase and increment in (Bi-2212andBi-2201and impurities) that's accumulation of which can cause defects in the internal structure of the compound .This agrees with other studies.[17,22].

It was noticed also a decrease in the peaks intensity for the doped specimen in comparison with that of the pure specimens .This is the same result of other study[22] in that doping by (La) change the high phase stability in (BSCCO). From estimation of lattice parameters (a,b,c) the results show an orthorhombic crystalline structure type . The change in (c) axis can be due to many causes, the first was the increment in (O_2) concentration that resulted from (La_2O_3) replacement instead of (CuO)and this increment will be taken by the double (Bi-O) layers which cause a stronger link because of the tertiary (La) valence that lead to increase ion bonding forces formed in the (Bi-O) layers and thus decrease the lattice parameter c , increase (a,b) , the rate c/a increase with (La) concentration as shown in figure (3).

The second reason was the effect of the surrounding environment on the preparation circumstances which has a great effect on oxygen concentration that's leads to change in phases and lattice parameters of superconductors[23].The third is that the difference in ionic radius can cause deformities in the lattice parameters.[24]which can be explained by substitution of (La)(117.2 pm) ionic radius instead of (Cu)of (87pm) ionic radius, as shown in Table(1).

In figure(4); electrical resistivity as a function of temperature for the system ($\mathbf{Bi_2Sr_2Ca_2Cu_{3-x}La_xO_{10+\delta}}$) at(x=0.05,x=o.1) shows a semiconductor behavior which can be due to the great decrement in Bi-2223 and increment in other phases (Bi-2212andBi-2201) in comparison with the pure specimen. This can be due to the absence of (Cu) in (CuO) layers due to (La) substitution which tends to do disorder in (CuO) lattice and cancelling the superconducting. Also increased or decreased (O_2) concentration in the mixture can be belonged to deformity in the bismuth oxide layers which expected to be opposed by increment in holes concentration in (Cu-O) layers ,hence there will be a rearrangement in holes concentration between (CuO and BiO) layers which can cause the change in lattice parameters and in holes concentration in (CuO) layer leading to a great decrement in the critical temperature,thus the superconductor (Tc) depends on the number of (CuO) layers and the (O_2) content in the specimen, so the specimens of high (T_C) contain high (O_2)content . [25]

The holes created in perovskite layers by increased Oxygen atoms in(CuO) layers will lead to shortening of bonds length in CuO and thus improvement or deterioration of (T_C). The relation between transition temperature for superconductors and holes concentration(p)can be calculated from equation(2):[19]

$p = 0.16-[(1-T_c/T_{c(max)})/82.6]^{1/2}$---------------(2)

where ($T_{C(max)}$) is a Critical Temperature of pure specimen, (T_C) Critical Temperature of doped superconductor.

The previous studies results show that Bi-2223 holes concentration range(0.116-0.16)[14]. From Table (2) , it was noticed that the doped specimens holes were less than the pure specimen holes and this leads to a decrease in T_C of the doped specimens. The holes concentration in (CuO) layers change with the increase of (La^{+3}) concentration and thus decreasing (T_C), which can be due to two reasons, the first is the structural instability and the other is the holes filling effect. This agrees with another study that substitution in (Cu) position leads to deterioration of the superconducting properties[16].

Conclusion

The XRD of the compound ($Bi_2Sr_2Ca_2Cu_{3-x}La_xO_{10+\delta}$) ,where (x=0.05,0.1,0.15,0.2) that's prepared by solid- state reaction method(SSR), shows that all the specimens have Orthorhombic crystalline structure.

(Bi-2223) concentration decreases by increasing (La)concentration in comparison with pure specimens while the electric resistivity investigation shows that the specimen of (La) concentration (0.05,0.1) has semiconductor behavior and the specimen of (La) concentration (0.15,0.2) has superconductor behavior with decrease in the critical temperature for specimen(0.15) at (Tc=115.8K),while the specimen (0.2)of(Tc=111K) in comparison with the pure specimen which has(Tc=120.9K).So we conclude that the structure and electrical properties for (Bi-2223)were very sensitive to doping with(La) leading to deterioration in superconducting properties due to substitution of (La^{+3}) instead of (Cu^{+2}).

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Table (1). The structural measurements value.

mixtures	**La_2O_3**	**H%**	**M%**	**L%**	**Impurities%**	**$T_{C(Offset)}$**	**$T_{C(Onset)}$**	**ΔT_C**	**$T_{C(mid)}$**	**Hole concentration**
O	0	84.115	7.249	2.665	5.970	120.9	125.1	4.2	123	0.16
A1	0.05	75.737	4.557	13.941	5.764	-----	-----	------	-----	------
A2	0.1	74.727	16.100	1.218	7.954	-----	-----	-------	-----	------
A3	0.15	83.796	4.542	2.372	9.288	115.8	117.1	1.3	116.45	0.137
A4	0.2	80.463	4.708	8.924	5.903	111	115.9	4.9	113.45	0.128

Table (2). Values of Critical Transition Temperature for all specimens.

Mixtures	(La_2O_3)	H%	M%	L%	Impurities%	$T_{C(OF)}$	a(Å)	b(Å)	C(Å)	C/a	ρ_M(gm/cm^3)	Structure
O	0	84.115	7.249	2.665	5.970	120.9	5.4169	5.4509	37.2246	6.871	2.250	Orthorhombic
A1	0.05	75.737	4.557	13.941	5.764	Semi	5.7061	5.4441	37.0341	6.490	2.16	Orthorhombic
A2	0.1	74.727	16.100	1.218	7.954	Semi	5.4230	5.4956	37.0022	6.823	2.28	Orthorhombic
A3	0.15	83.796	4.542	2.372	9.288	115.8	5.4030	5.4376	37.0181	6.851	2.33	Orthorhombic
A4	0.2	80.463	4.708	8.924	5.903	111	5.4410	5.8173	36.8927	6.780	2.18	Orthorhombic

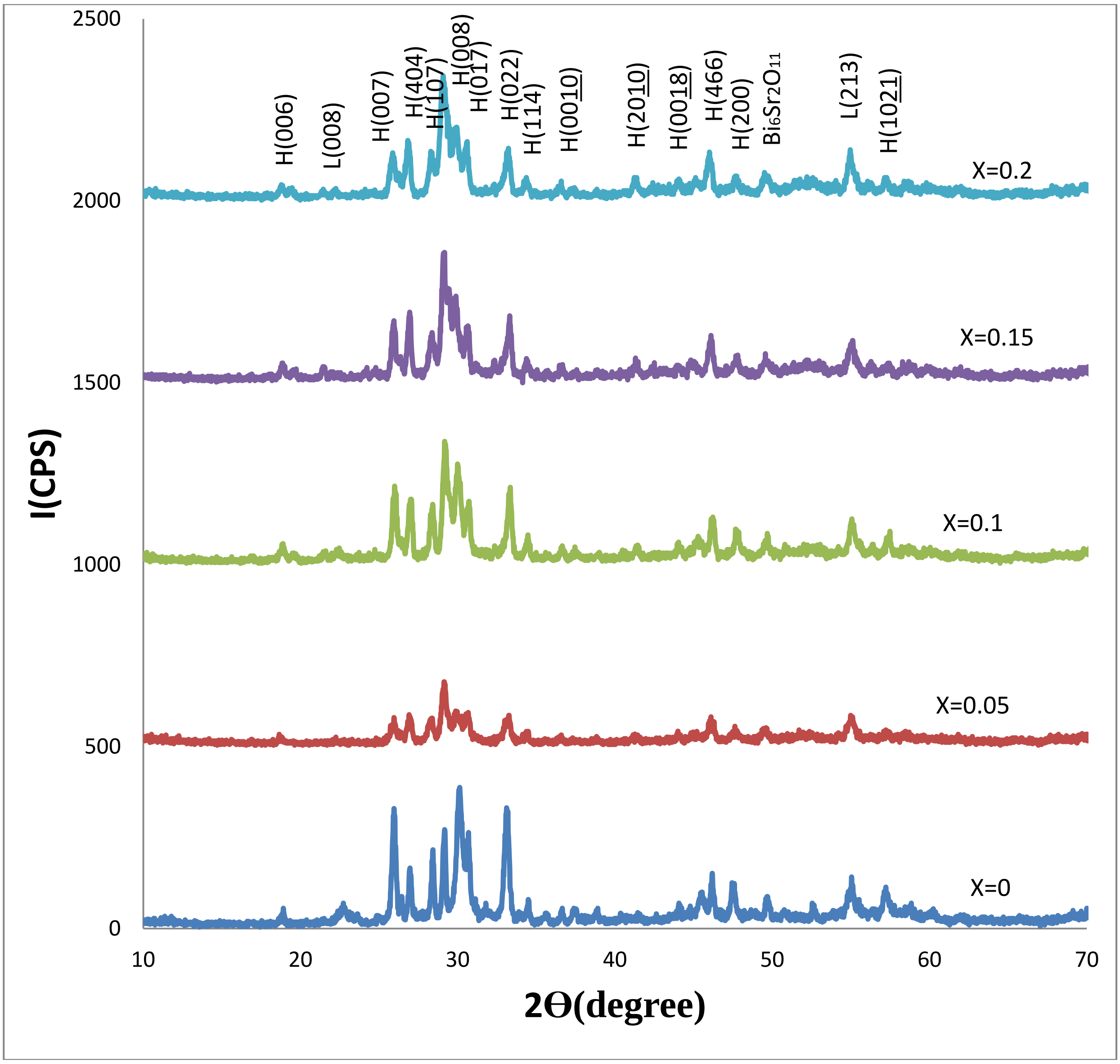

Figure (1).(XRD)pattern of all specimens.

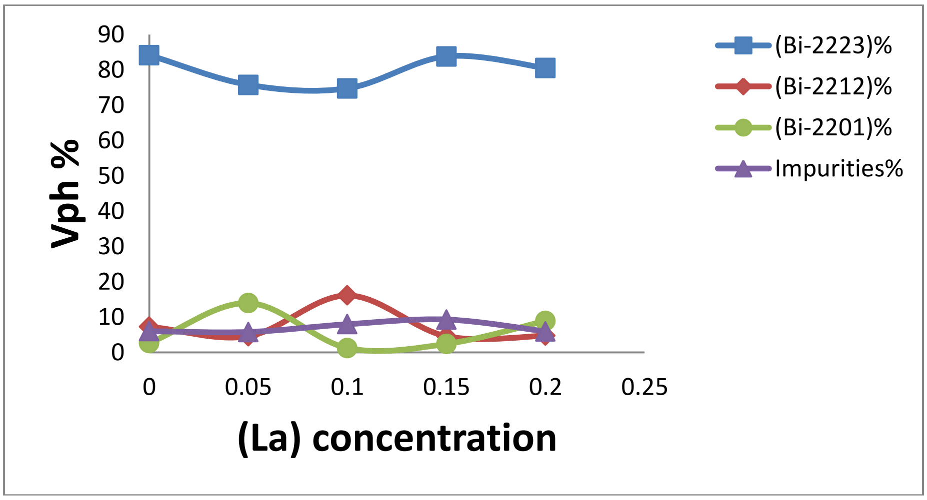

Figure (2).The volume fraction of all phases and impurities as a function of (La)concentration.

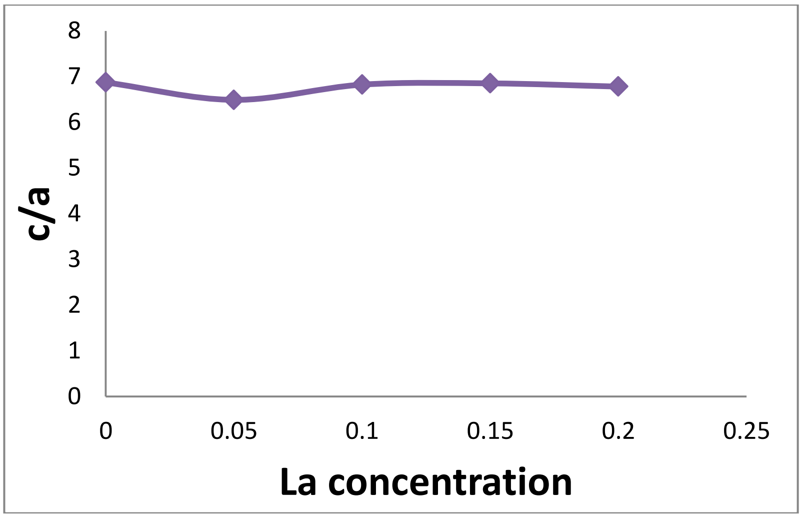

Figure (3).The ratio of lattice parameter (c/a) as a function of (La) concentration.

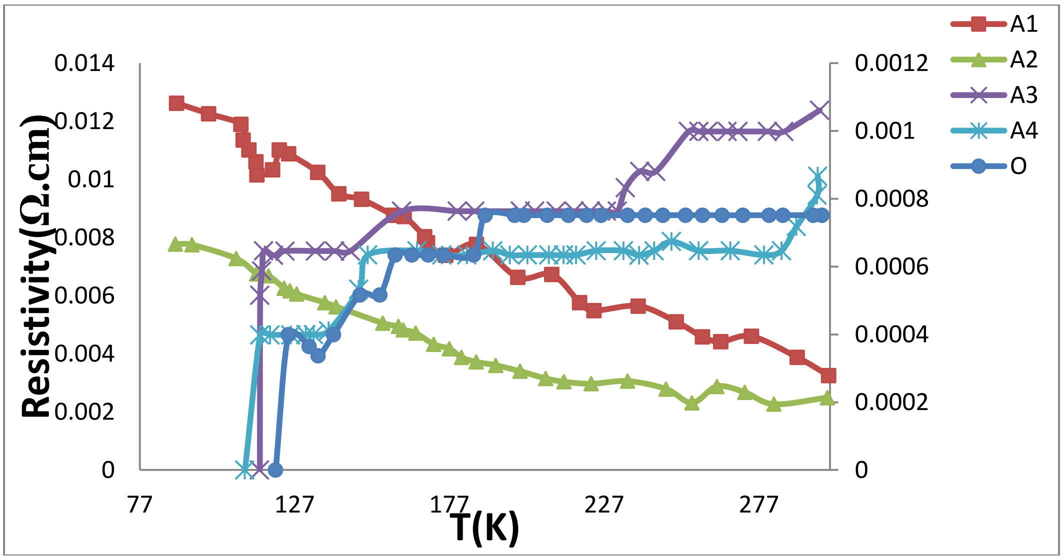

Figure (4).Electrical resistivity as a function of temperature under cooling by liquid Nitrogen,(right perpendicular axis refers to the(O,A3,A4).