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Effect of Sintering Temperature on $Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$ Superconductors

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Abstract

High temperature superconductors with a nominal composition $Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$ for ($0\leq x\leq 0.5$) was prepared by solid state reaction method. The effect of sintering temperature and substitute of Cu on $Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$ compound has been investigated by X-ray diffraction , resistance measurements and oxygen content to obtain the optimum conditions for the formation and stabilization of the high T_C phase (2223- phase).The results showed that the optimum sintering temperature for the composition $Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$ is T_s=860˚C for t_s=140h.

The x-ray diffraction (XRD) analysis showed that all the samples have almost two phases: high-T_c phase (2223- phase) and low-T_C phase (2212- phase) in addition to the existing of very low phase in the sample x=0.4. It was found that all the samples having an orthorhombic structure with lattice parameter value (c) increased with increasing of the critical temperature T_c.

Substitution of Cu to 0.2, 0.3, 0.4 will increase the transition temperature to T_C=127K, 130K, 125K, respectively with increasing oxygen content.

Introduction

It has been reported that a Bi-Sr-Ca-Cu-O superconductor has two superconducting phases of both high T_c and lower T_c. A number of discussions have been made particularly on the high T_c phase. Major understanding up to present is that the high T_c phase may correspond to triple Cu-O layers sandwiched by Bi_2O_2 layers [1-2].

The crystal structures of the members of homologous series, $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$, are similar to the other high temperature superconducting cuprate systems [3]. The bismuth compound can be described by the formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ where n=1, 2 and 3. Three perovskite related oxide have been isolated by Tarascon *et al.*, [3], $Bi_2Sr_2CuO_6$ (n=1, 2201 phase, $T_c\leq 20$K), $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (n=2, 2212 phase, T_c=85K) and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (n=3, 2223 phase, T_c=110K) are formed by convential sintering method. The structure consists of perovskite-like units containing one, two or three CuO_2 planes sandwiched between Bi-O bilayers.

The crystal structures of Bi-based superconductors consist of two generic building blocks [4]: the vital, superconducting copper-oxide layers or planes, and the insulating block layers which can act as electronically active charge-reservoirs for hole or electron donation to the copper-oxygen layers.

The copper-oxide layers can be thought of as being derived from the perovskite structure-type by denticulation of oxygen from between the copper-oxide planes, while the insulating block is derived from the rock-salt structure [4]. The lattice parameters of the fundamental unit cells, determined by X-ray diffraction, are as follows: $a = 5.383\,\overset{\circ}{A}$, $b = 5.390\,\overset{\circ}{A}$ and $c = 24.38\,\overset{\circ}{A}$ for 2201-phase; $a = 5.395\,\overset{\circ}{A}$, $b = 5.390\,\overset{\circ}{A}$ and $c = 30.65\,\overset{\circ}{A}$ for 2212-phase and $a = b = 5.4\,\overset{\circ}{A}$ and $c = 37\,\overset{\circ}{A}$ for 2223-phase. The substitution of cations frequently occurs in these phases. The values of these parameters changes slightly depending on the cationic substitution.

Recently, the variation of hole concentration by cation substitution is increasingly used to investigate the mechanism of high T_c superconductivity in the cuprate oxides. Partial substitution for Bi^{+3} by ions of various radii and valance such as Pb^{+2} in $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ compound may be affect the high T_c- phase formation, chemical stability and the superconducting properties [5-6].

Experimental

The system ($Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$) with ($0 \leq x \leq 0.5$) was prepared by solid state reaction method. First of all the molar ratios of high purity powders of Bi_2O_3, Pb_3O_4, $Sr(NO_3)_2$, $CaCO_3$ and CuO were adjusted, mixed using agate mortar. This mixture was then calcined in a tube furnace under atmospheric conditions that has programmable controller type [Eurotherm 818P] for 20-24 hours at 800°C with a rate of 2°C/min. Then pressed into pellets of 1.3 cm in diameter and (0.25-0.28) cm thick, by using a manually hydraulic press type (SPECAC) under pressure of 0.5GPa. These pellets were sintered in air atmosphere at sintering temperature T_s= (860 and 870) °C for 140 h with a rate of 2°C/min by using furnace that has programmable controller type [Eurotherm 818P]. Then the pellets cooled to room temperature with the same rate of heating.

All samples in the present investigations were subjected to gross structural characterization by X-ray diffraction (XRD) type (Siemens D500)[Italia], XRD 6000 (SHINADZU)[Iraq]. he DC electrical resistance was measured with the four- probe technique [7-8]. Iodometric titration was used to access the oxygen content in the samples [9].

Results

The resistivity versus temperature for the nominal composition $Bi_{2-x}Cu_xPb_{0.3}$ Sr_2Ca_2 $Cu_3O_{10+\delta}$ for ($0 \leq x \leq 0.5$) which sintered at 860°C and 870°C for 140h under atmospheric conditions are plotted in Fig. (1). From this figure the resistivity decreasing nearly linearly with decreasing temperature, while that for the sample (x=0.3) sintered at 870°C get semiconducting behavior. This agrees with the results of the researcher Hermiz [10]. However the resistivity of the samples sintered at 860°C with (x=0.0, 0.2, 0.3 and 0.4) showed a superconducting behavior with zero resistivity at the temperature of T_c=(100,127,130,125)K respectively, while for the same samples sintered at 870°C did not reach to zero-resistivity.

The samples sintered at 860°C have normal state resistivity lower than that the same samples sintered at 870°C this can be attributed to crack formation as a result of excessive mechanical deformation.

From the above results we can conclude that the sintering temperature is considered to be critical value for the high-T_c phase formation.

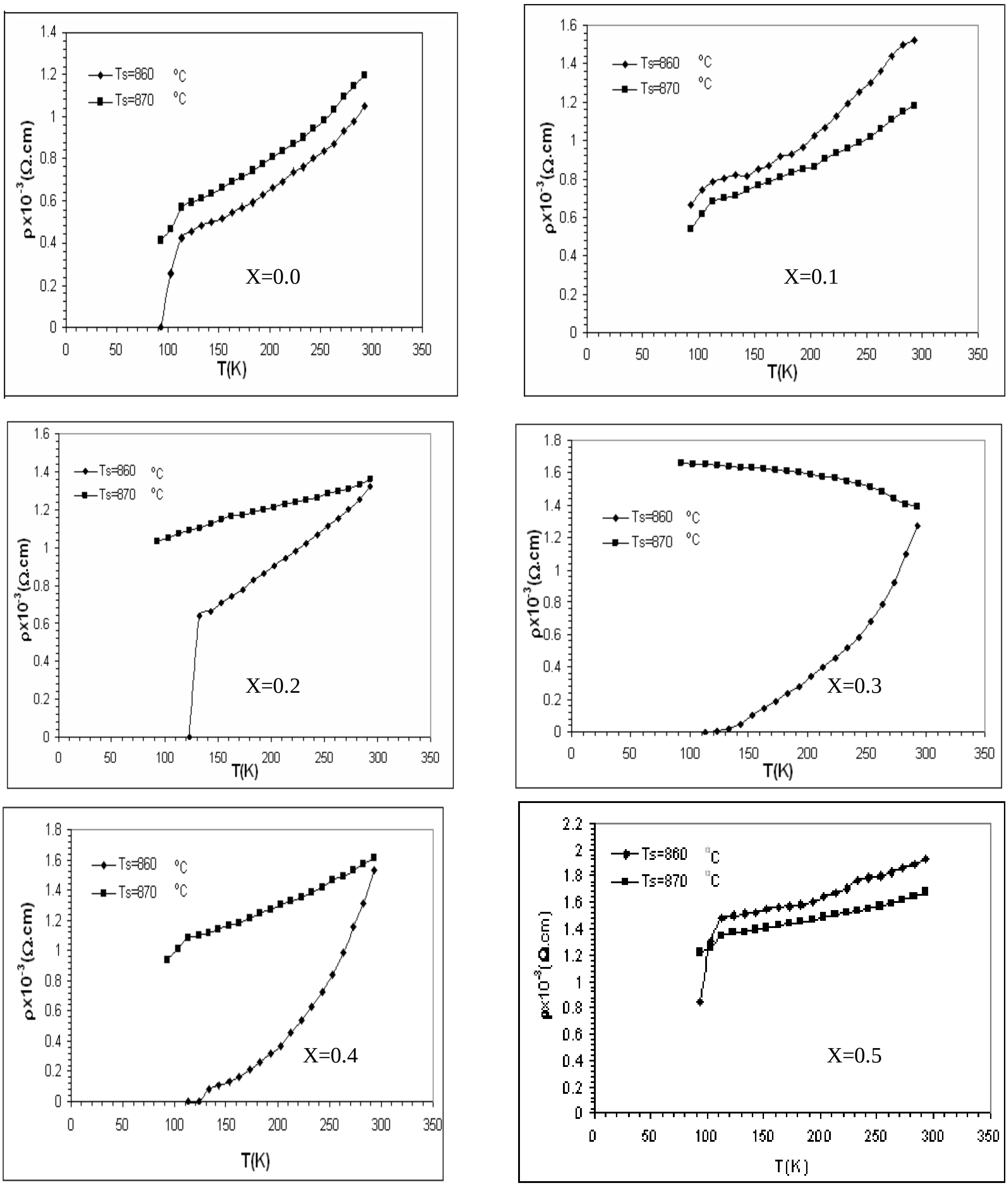

Fig. (1) Temperature dependence of resistivity for $Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$ with different x ($0 \leq x \leq 0.5$) sintered at different temperature for t_s=140h.

Effects of Cu substitution on the result of electrical resistivity measurements were investigated. The resistivity versus temperature for samples with nominal composition $Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$ for ($0 \leq x \leq 0.5$) sintered at 860^{o}C and 870^{o}C for 140h as shown in Fig (1). It is found from these figures that compound at x=0.0 has $T_{c(onset)}$=110K and $T_{c(offset)}$=90K. A sharp drop of resistivity was observed for the composition has x=0.2 with $T_{c(offset)}$=125K and $T_{c(onset)}$=130K. The sharp drop at the transition temperature is due to transition within grains and the presence of low-T_c (2212) phase [11]. For the composition that has (x=0.3, 0.4) the superconducting transition were not sharp and they had $T_{c(offset)}$=110K and $T_{c(onset)}$=150K, $T_{c(onset)}$=140K respectively. However the sample with (x=0.3,x=0.2) shows a sharp decrease with decreasing temperature, revealing that the sample consists predominantly of (2223) phase, this trend is also a good evidence of the homogeneity of the (2223) phase [11]. At (x=0.1,x=0.5) the resistivity decreases nearly linearly with decreasing temperature.

The XRD measurement were carried out on the most samples and most of them showed two main phases, i.e., high-T_c phase (2223), low-T_c phase (2212) and very low-T_c phase (V.L.T.P) in the sample with x=0.4.

X-ray diffraction patterns for all specimens with Miller indices of orthormbic structure are shown in Figs. (2,3). It should be noted that the relative intensity of diffraction peaks varies slightly with different samples while peak positions can move with increasing of Cu content, which change the lattice constant of the sample.

From these figures we can notice that the sum intensity of the high-T_c phase reflections is greater than those of the low-T_c phase with appearance of some of peaks belong to high phase (2223). This case appears more clearly with increasing Cu content, and it indicates the increasing of the crystalline arrangement degree[12].

A computer program was used as a helpful tool for the determination of the lattice parameters. The lattice constants (a, b, c) and cell volume (V) of the prepared samples listed in Table (1) and Table (2).

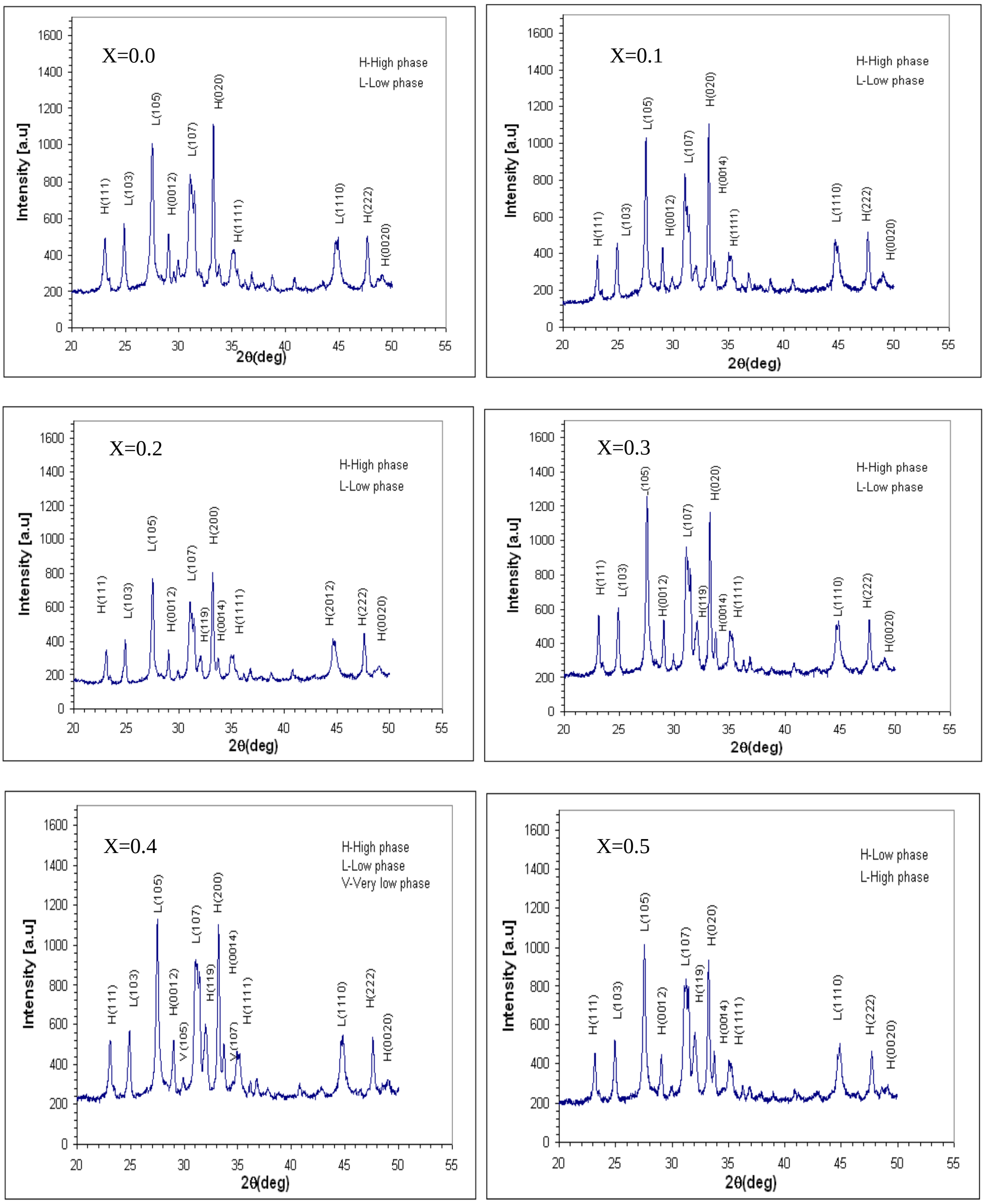

Fig. (2) XRD patterns for the samples with (0≤x≤0.5) at T_s=860°C for 140h.

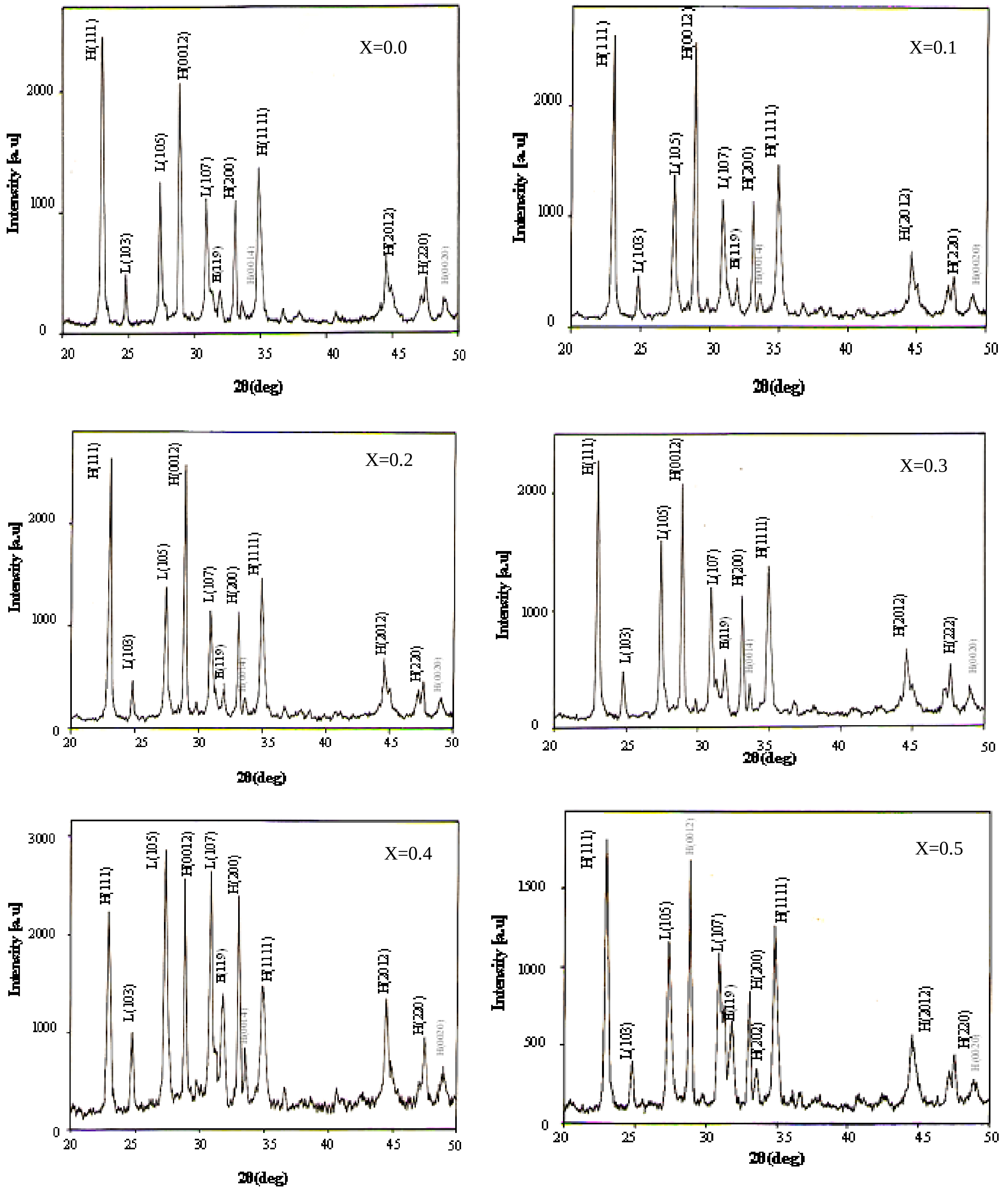

Fig. (3) XRD patterns for the samples with $(0\leq x\leq 0.5)$ at $T_s=870^oC$ for 140h.

Table (1)

Values of lattice parameter, unit cell volume, oxygen content and values of T_C for different x sintered for 140 h at 860°C .

x	*a* (Å)	*b* (Å)	*c* (Å)	*V*(Å)^3	*δ*	T_C(K)
0.0	5.4759	5.3830	37.0553	1092.2705	-0.5595	100
0.1	5.4879	5.3758	37.1231	1095.2002	-0.4274	<77
0.2	5.3836	5.4633	37.1068	1091.3934	-0.3705	127
0.3	5.4740	5.3883	37.1453	1095.6212	-0.3155	130
0.4	5.3893	5.4450	37.0952	1088.5489	-0.4023	125
0.5	5.4547	5.3848	37.1362	1090.7818	-0.5555	<77

Table (2)

Values of lattice parameter, unit cell volume, oxygen content and values of T_C for different x sintered for 140 h at 870°C .

x	*a* (Å)	*b* (Å)	*c* (Å)	*V*(Å)^3	*δ*	T_c(K)
0.0	5.3840	5.4376	37.2369	1090.1489	-0.6328	<77
0.1	5.3842	5.4347	37.1777	1087.8757	-0.5	<77
0.2	5.3860	5.4325	37.1808	1087.8895	-0.7277	<77
0.3	5.3771	5.4774	37.1738	1094.8623	-0.1733	Semi.
0.4	5.3842	5.4347	37.1777	1087.8757	-0.0514	<77
0.5	5.3808	5.4348	37.2363	1088.9224	-0.2112	<77

From those Tables, we can see a randomly variation in both of a- and c- lattice constant with the increasing of Cu content and this behavior may be explained by the differences in the ionic radii for both of Cu and Bi, which resulted in the c-axis elongation, then heightening of the high-T_c phase and hence increase its T_c rapidly, as it is mentioned previously.

The change in the c lattice parameter is related to the distribution of holes between bismuth oxides layers and CuO planes. The doped ions may change the spacing between the CuO layers and thus affect the charge transfer to the CuO layers [11]. A high shift in peaks position and some of the peaks disappeared when increasing the sintering temperature to 870°C with losing the high T_c superconducting state as shown in the Table (2).

However, both of c-axis and T_c increased, this reveals the increase in δ values as we will see later.

The oxygen content δ for all samples were calculated and listed in Table (1) and Table (2). The variation of T_c is associated with δ [13,14]. It can be noticed that T_c varies in accordance to the variation of (δ) for different values of x. Both (δ) and T_c increased with increasing x to x=0.2 and 0.3, then reduced for further increasing of x. It has been suggested [15, 16] that T_c is related to the percentage of Cu^{+3} present in the compound. So we expect that the increasing of x up to 0.2 will increase the amount of Cu^{+3} with respect to other valences, (Cu^{+2} and Cu^{+1}). It has been pronounced that holes are present on oxygen rather than on copper [17]. Similar behavior of (δ) with the transition temperature for $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_\delta$ system was indicated by Zhao *et al.*[18].

Conclusions

Cu doped Bi-based HTS have been prepared by solid state reaction. The structure was orthorhombic with high ratio of Bi-2223 superconductor phase.

In general, substitution Cu at Bi site enhanced T_c to 127,130 , and 125K with 0.2,0.3, and 0.4 respectively. In addition, oxygen content δ have been found increases with increasing Cu concentration.

Acknowledgments

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الخلاصة

حُضرت المركبات $Bi_{2-x}Cu_xPb_{0.3}Sr_2Ca_2Cu_3O_{10+\delta}$ الفائقة التوصيل ولقيم $(0\leq x\leq 0.5)$ بطريقة تفاعل الحالة الصلبة. تمت دراسة تأثيرات التعويض الجزيئي للبزموث بالنحاس كما درست أيضاً تأثيرات درجة حرارة التلبيد بواسطة تقنية حيود الأشعة السينية (XRD)، قياسات المقاومية الكهربائية ومحتوى الاوكسجين، لغرض الحصول على الظروف ال مثلى لتكوين واستقرار الطور الفائق التوصيل ذو الدرجة الحرجة العالية (2223-phase). لقد بينت نتائجنا إن ظروف التلبيد المثلى للمركب النقي والمعوض هي درجة حرارة تلبيد مساوية إلى 860 درجة مئوية . أوضحت نتائج تحليلات الاشعة السينية (XRD) بأن للمركب طورين: الطور الفائق التوصيل العالي (2223- phase) والطور الفائق التوصيل الواطئ (2212- phase) مع وجود طور الفائق التوصيل الواطئ جدا في العينه $x=0.4$ وان جميع العينات لها تركيب (معيني) واظهرت هذه التحليلات زيادة في قيمة الثابت c مع زيادة درجة الحرارة الحرجة T_c. وقد وجد إن التعويض بالنحاس وبالنسب (0.2 و 0.3 و 0.4) يعمل على رفع درجة الحرارة الحرجة T_c إلى (127 و 130 و 125) كلفن على التوالي مع زيادة محتوى الأوكسجين في المركب