

Effect of $(\text{CuPb})_x$ Substitution on T_c of $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ Superconductors

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ABSTRACT

High temperature superconductors with a nominal composition $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ for $(0 \leq x \leq 0.5)$ were prepared by solid state reaction method. The effect of $(\text{CuPb})_x$ substitution on T_c of $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ 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 $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ is $T_s=1133\text{K}$ for $t_s=140\text{h}$.

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). 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 $(\text{CuPb})_x$ to 0.1, 0.3, 0.4 increases the transition temperature to $T_c=107\text{K}$, 125K , 95K , respectively.

تأثير التعويض ب $(\text{CuPb})_x$ على مركبات $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ الفائقة التوصيل

الخلاصة

حضرت المركبات $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ ($0 \leq x \leq 0.5$) بطريقة تفاعل الحالة الصلبة. تمت دراسة تأثيرات التعويض الجزئي للبريوم، كما درست أيضاً تقنية حيود الأشعة السينية (XRD)، قياسات المقاومة الكهربائية ومحتوى الاوكسجين، لغرض الحصول على الظروف المثلى لتكوين واستقرار الطور الفائق التوصيل ذو الدرجة الحرجة العالية (2223-phase). لقد بينت نتائجنا ان ظروف التليد المثلى للمركب النقي والمعووض هي درجة حرارة تليد 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) وان جميع العينات لها تركيب (معيني) واطهرت هذه التحليلات زيادة في قيمة ثابت الشبكة c مع زيادة درجة الحرارة الحرجة T_c . وقد وجد ان التعويض ب $(\text{CuPb})_x$ وبالنسب (0.1 و 0.3 و 0.4) يعمل على رفع درجة الحرارة الحرجة T_c إلى (107 و 125 و 95) كلفن على التوالي.

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, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$, are similar to the other high temperature superconducting cuprate systems [3]. The bismuth compound can be described by the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ where $n=1, 2$ and 3 . Three perovskite related oxide have been isolated by Tarascon *et al.*, [3], $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ ($n=1$, 2201 phase, $T_c \leq 20\text{K}$), $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ ($n=2$, 2212 phase, $T_c=85\text{K}$) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ ($n=3$, 2223 phase, $T_c=110\text{K}$) are formed by conventional 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.

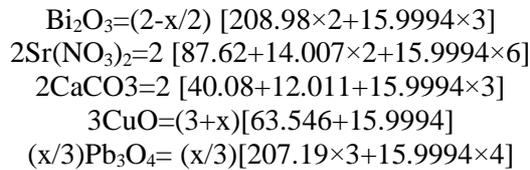
The copper-oxide layers can be thought of as being derived from the perovskite structure-type by denticulation of oxygen from between the copper-oxide planes, while the insulating block is derived from the rock-salt structure [4]. The lattice parameters of the fundamental unit cells, determined by X-ray diffraction, are as follows: $a = 5.383 \text{ \AA}$, $b = 5.390 \text{ \AA}$ and $c = 24.38 \text{ \AA}$ for 2201-phase; $a = 5.395 \text{ \AA}$, $b = 5.390 \text{ \AA}$ and $c = 30.65 \text{ \AA}$ for 2212-phase and $a = b = 5.4 \text{ \AA}$ and $c = 37 \text{ \AA}$ 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 $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ compound may be affect the high T_c - phase formation, chemical stability and the superconducting properties [5-6].

The important role of Cu and Pb in oxides superconductors, thus we find it is interesting to investigate the effect of partial substitution $(\text{CuPb})_x$ at Bi sites, on the formation of the high- T_c phase in the $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ compounds with ($0 \leq x \leq 0.5$) to find the best compound of the samples as well as we need to get highest T_c that possible to bring these superconducting compounds into more useful forms.

EXPERIMENTAL

Since Cu and Pb play an important role in oxides superconductors, thus it is interesting to investigate the effect of partial substitution of (CuPb) at the Bi sites, on the formation of the high- T_c phase, in the $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ compounds. The system $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ with ($0 \leq x \leq 0.5$) was prepared by solid state reaction method. The total weight of the compounds was taken as follows:



First of all the molar ratios of high purity powders of Bi₂O₃, Pb₃O₄, Sr(NO₃)₂, CaCO₃ 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 °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 XRD 6000 (SHINADZU) was used Cu_{Kα} source. The DC electrical resistance was measured with the four- probe technique [7-8].

The two outer probes is used to carry the current by using D.C power supply type (Philips PE 1537) while the inner probes (middle probes) is used to reading the voltage between the middle probes (the voltage on the sample) by using a digital nanovoltmeter type (Keithely 180-digital) with sensitivity of about (± 0.1 nanovolt).

The sample was fixed in liquid nitrogen cryostat instrument which was join to a rotary pump (Edwards) to get a vacuum with pressure of 10⁻² mbar inside the cryostat, and join also to a sensor of a digital thermometer type (Doric 450) with sensitivity of about (±1°C) near the sample position by thermocouple. Iodometric titration was used to access the oxygen content in the samples [9].

RESULTS AND DISCUSSIONS

If a current I is passing through the sample and V is the voltage drops across the electrodes then the resistivity ρ of the sample can be calculated according to the following equation.

$$r = 0.4532 \frac{V}{I} \text{ (}\Omega\text{.cm)}$$

The resistivity versus temperature for the nominal composition Bi_{2-x}(CuPb)_xSr₂Ca₂Cu₃O_{10+δ} for (0≤x≤0.5) which sintered at 860°C for 140h under atmospheric conditions are plotted in Figs. (1). From this figure the resistivity decreasing nearly linearly with decreasing temperature, while that for the sample (x=0.0) sintered at 860°C get semiconducting behavior. This agrees with the results of Hermiz [20]. However the resistivity of the samples sintered at 860°C with (x=0.1, 0.3, 0.4) showed a superconducting behavior with zero resistivity at the temperature of T_c=(107,125,95)K respectively, while for (x=0.2, 0.5) did not reach to zero-resistivity. This may be attributed to crack formation as a result of excessive mechanical deformation.

Effects of (CuPb)_x substitution^[19] on the result of electrical resistivity measurements were investigated. The resistivity versus temperature for samples with nominal composition Bi_{2-x}(CuPb)_xSr₂Ca₂Cu₃O_{10+δ} for (0≤x≤0.5) sintered at 860°C for 140h as shown in Figs (1). It is found from these figures that compound at x=0.1 has T_{c(onset)}=110K and T_{c(offset)}=105K. The sharp drop at the transition temperature is due to transition within grains and the presence of low-T_c (2212) phase^[10]. For the composition that has (x=0.3) the superconducting transition were not sharp and they had T_{c(offset)}=110K and T_{c(onset)}=140K. However the sample with (x=0.1,x=0.3,x=0.4) 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^[10].

At (x=0.5,x=0.2) the resistivity decreases nearly linearly with decreasing temperature. It seems that Pb does not enter the Cu or Ca site. Pb seems to partially occupy the Bi site in general features^[11]. Chemical formulate of the analyzed compound can be formulated by normalizing numbers of cations on the basis of the number of Cu atoms in unit cell^[12].

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).

X-ray diffraction patterns for all specimens with Miller indices of orthorhombic structure are shown in Figs. (2). From these figures it is noticed that the relative intensity of the diffraction peaks vary with different samples while peak positions varies slightly with increasing the (CuPb) content (which causes the lattice constant of the sample to change). The impurity phases was observed in all the samples Ca₂CuO₃, CuO and Ca₂PbO₃ appear at 2θ=36.3, 2θ= 38.4 and 2θ=35.3, respectively. The appearance of impurity phases as a result of excess Ca and Cu elements.

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).

From this Table, we can see a randomly variation in both of a- and c- lattice constant with the increasing of (CuPb) 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.

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^[10]. The variation of oxygen content in these compounds are shown in Table (1).

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. 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 0.1 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].

CONCLUSIONS

(CuPb) 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 (CuPb) at Bi site enhanced T_c to 107, 125, and 95K with 0.1, 0.3, and 0.4 respectively. In addition, that T_c varies in accordance to the variation of (δ) for different values of x .

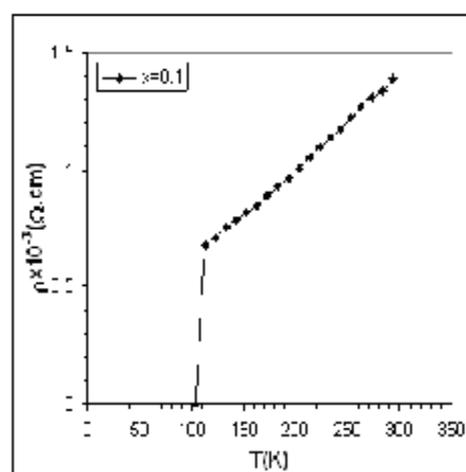
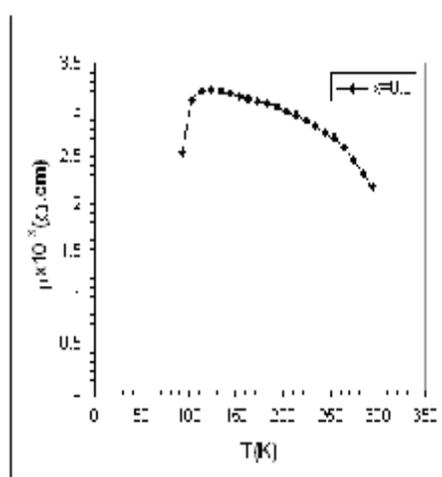
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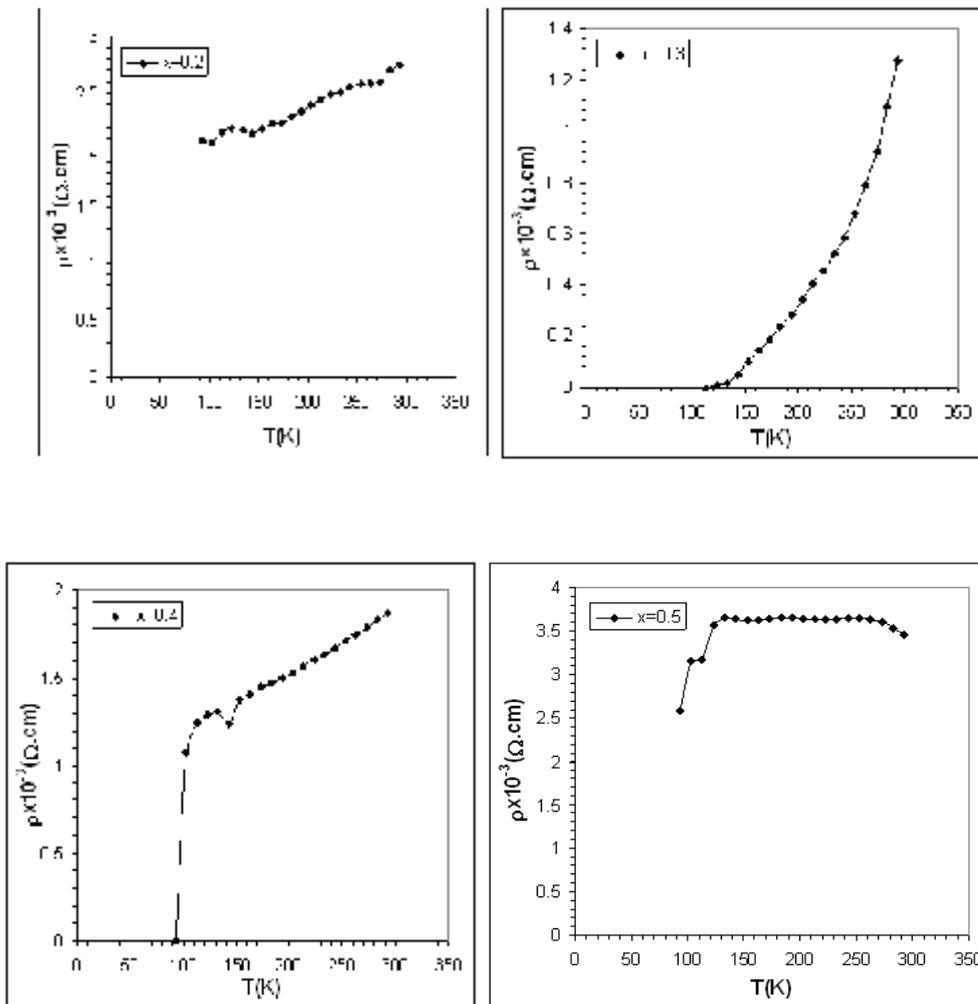
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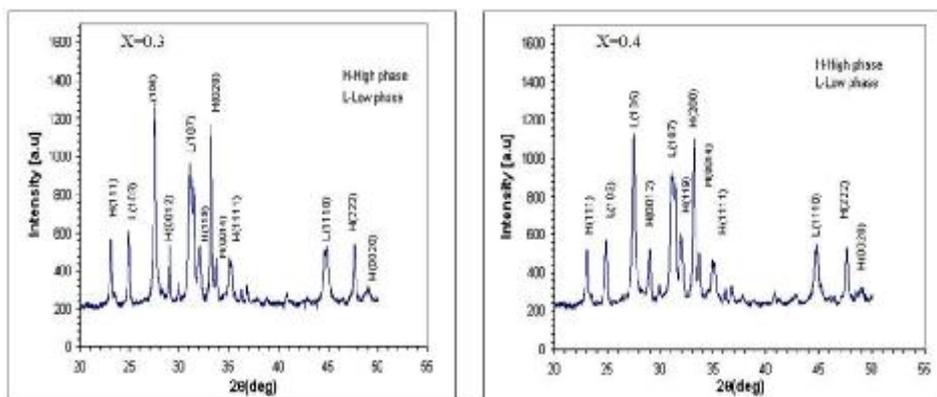
Table (1) Values of lattice parameter (a,b,c), unit cell volume(V), oxygen content (δ) and values of T_C for different x sintered for 140 h at 860°C .

x	a (Å)	b (Å)	c (Å)	V(Å) ³	δ	T _C (K)
0.1	5.379	5.428	37.1231	1083.8910	0.123	107
0.3	5.4740	5.3883	37.1453	1095.6212	-0.3155	125
0.4	5.2233	5.4350	37.0123	1055.9209	0.1125	95





Figures (1): Temperature dependence of resistivity for $\text{Bi}_{2-x}(\text{CuPb})_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ sintered at $T_s=860^\circ\text{C}$ for $t_s=140\text{h}$.



Figures (2): XRD patterns for the samples with $(0 \leq x \leq 0.5)$ at $T_s=860^\circ\text{C}$ for 140h.