

Influences of K Substitution on Bi (Pb)-2223 Superconductors

Muna Moussa Abbas, Huda Deia Dehi

Abstract— Solid state thermodynamically reaction method were used to prepare a high temperature superconductor (HTSC) with a nominal composition $\text{Bi}_{2-x}\text{K}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ with $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 . The phase identification /gross structural characteristics of synthesized HTSC compounds explored through X-ray diffractions. The results reveal that all samples are polycrystalline and both (Bi, Pb)-2223 and -2212 phases coexist in the samples having orthorhombic crystal structure. The volume fraction was estimated from the intensities of Bi-(2223) and Bi-(2212) phases. The lattice constants of samples were determined from the XRD analysis by indexing the peaks observed for (Bi, Pb)-2223 phase. The electrical resistivity results showed a significant influence of the K substitution on Bi (Pb)-2223 superconductors and the highest T_C at 128K with $x=0.5$.

Index Terms— Bi-based superconductors, K substitution, Phase formation, solid state reaction.

I. INTRODUCTION

Bi-based compounds are considered to be the most promising material for the application of high- T_C superconductors. There are three superconducting phases in the BiSrCaCuO system which have an ideal structural formula $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n-1}\text{Cu}_{n0+2n}$, with $n = 1, 2$ or 3 indicating the number of the CuO_2 planes. Synthesis of a nearly pure single-phase high- T_C 2223 phase ($T_C \approx 110\text{K}$) is a complicated process due to its extremely narrow stability range [1]. The low T_C phase (2212) has more stable structure than the other phases and during the (2223) phase formation some fraction of the material may be in the low T_C phase [2]. The superconducting properties of BiSrCaCuO compounds can be controlled by the addition or substitution of the elements with different ionic radius and different bonding characters [3]. It was established that the doping of elements (Pb, Fe, Co, Ni, V, Zn) in Bi-based superconducting has been affected the superconducting properties with increase of the amount of doping, regardless of the nature of the dopants. The repression of superconductivity was concluded to be due to local disorder induced by the amount of doping [4]. Among these, addition or partial substitution of trivalent Bi with Pb is the most effective method to enhance the formation of the Bi-2223 phase [5 and 6]. Hermiz *et al.* [7] prepared high- T_C phase $(\text{Bi}_{0.7}\text{Pb}_{0.3})_2\text{Ag}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ showed that the higher Ag content $x=0.5$ favor the formation of the 2223 phase and

increase T_C to 105K. Meretl *et al.* [8] established that addition of alkaline metals to Bi2223 compounds leads to a complex change of the physical properties of superconductors. They observed single superconducting transition with T_C 110K for $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.7}\text{K}_{0.3}\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductor. Oboudi *et al.* [9] found that doping Bi2223 compounds with Li enhances the superconductor properties and showed the highest T_C -zero at 130K for $\text{Bi}_{1.7}\text{Li}_{0.3}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductor. Petrashko *et al.* [10] investigated how the partial replacement of oxygen with fluorine and of strontium with potassium influences the formation and properties of the formation; the reaction enters the stage of crystal growth. The influence of the atomic substitution or doping is not yet fully understood in the cuprate superconductors, and this represents our active area of the current research to investigate the influence of potassium on the formation of superconducting phases in a bismuth system, and on the variation of its physical properties.

II. EXPERIMENTAL PART

$\text{Bi}_{2-x}\text{K}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples with $0 \leq x \leq 0.5$ were prepared by the conventional solid state reaction method. Appropriate amounts of high purity powders of $\text{Bi}_2(\text{CO}_3)_3$, PbO , $\text{Sr}(\text{NO}_3)_2$, CaO , CuO and K_2CO_3 were used as starting materials. The powders of precursor were mixed together by using agate mortar. A sufficient quantity of 2-propane was used to homogenize the mixture. The mixture was grounded to a fine powder and then calcined in air by using a tube furnace at 800°C for 24hr. The powder pressed into disc-shaped pellets with 13mm in diameter and (20-30) mm thickness using a manually hydraulic press type (Specac) under different pressures around 0.5 GPA. After that pellets sintered at 850°C for 140hr then air cooling to room temperature. All samples in the present investigation were subjected to gross structural characterization by X-ray diffraction (XRD). The DC electrical resistance was measured with the four probe technique at temperature range (77-300) K to determine the critical temperature (T_C).

III. RESULTS AND DISCUSSION

The XRD patterns of the $\text{Bi}_{2-x}\text{K}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ for ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.5) samples indicated that all samples are polycrystalline and correspond to orthorhombic structure. Two main phases, i.e., high- T_C phase (2223) and low- T_C phase (2212) are obtained with some impurities phases like $\text{Sr}_2\text{Ca}_2\text{Cu}_7\text{O}_8$ detected at 2θ equal to 36.3° [11] as shown in Figure 1.

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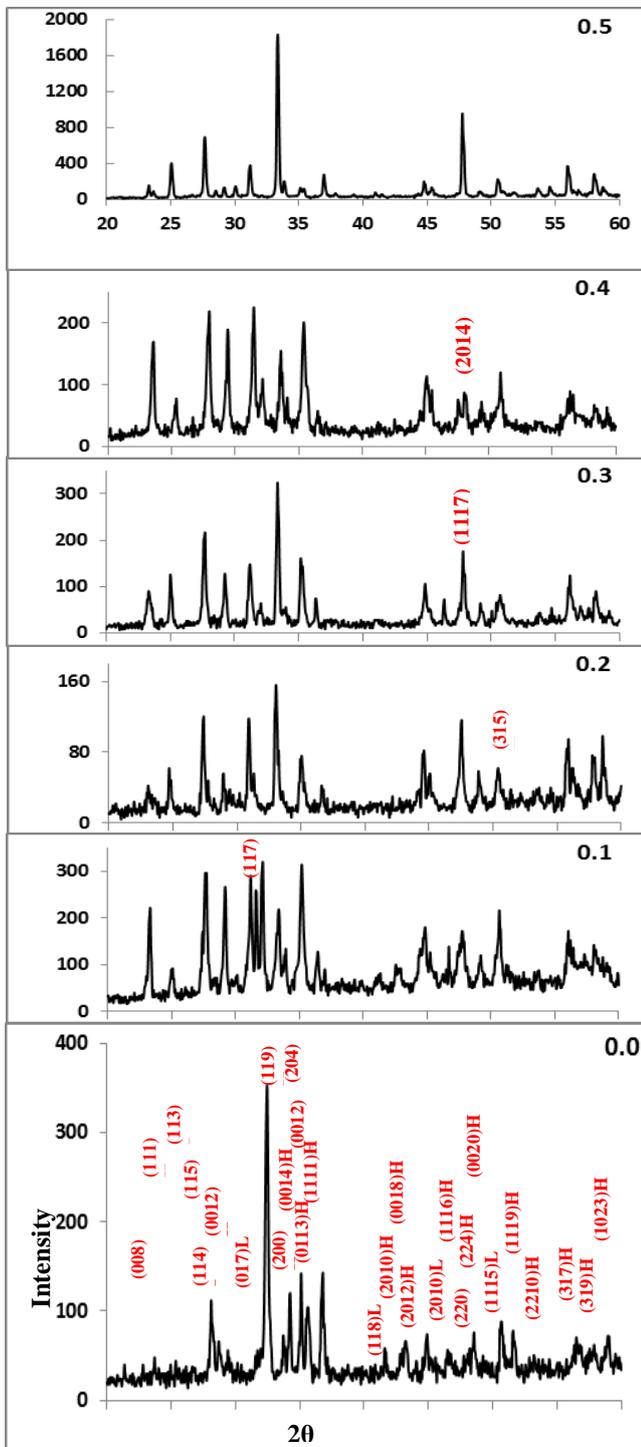


Figure 1: XRD patterns of $\text{Bi}_{2-x}\text{K}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ superconductors.

The occurrence of all those non-superconducting impurity phases will lead to a reduction of the critical temperature T_C of the samples. It can be notice that all the samples studied by XRD measurements were mainly consisting of (2212) and (2223) phases, with the (2223) phase being the dominant one. The appearance of more than two phases could be related to the stacking faults along the c-axis. It should be noted that the relative intensity of the diffraction peaks vary with different samples while peak positions varies slightly with increasing the K content likewise, resulted, a change in the lattice constant of the sample. Interestingly, the most intense peak pattern of samples belongs to the high- T_C phase due to the enhanced grain growth and better orientation of grains with K diffusion especially at $x=0.5$. According to the model suggested by Grivel and Fliikiger, the (Bi,Pb)-2223 phase

forms not due to a layer-by layer intercalation in the pre-existing (Bi,Pb)-22 12 grains but through a distinct nucleation and growth process[12]. Thus the substitution by K improves the crystalline arrangement degree and volume fraction of the 2223 phase [11and 13]. The relative volume fractions of the Bi-2223 and Bi-2212 phases were estimated from the peak intensities of the same particular reflections, using the following formulas [14]:

$$\text{Bi-(2223)\%} = \frac{\sum I(2223)}{\sum I(2223) + I(2212)} \times 100$$

$$\text{Bi-(2212)\%} = \frac{\sum I(2212)}{\sum I(2223) + I(2212)} \times 100$$

Where: I (2223) and I (2212) are the intensities of Bi-2223 and Bi-2212 phases respectively. The calculated relative portion of all samples is listed in Table 1 and shown in figure 2. Meanwhile, the highest 2223-phase fraction is observed for undoped sample; it had been shown the substitution with K in combination with Pb promotes formation of high- T_C phase 2223. This is due to improvement of the nucleation.

Table 1: Bi-(2223) and Bi-(2212) phases volume fraction $\text{Bi}_{2-x}\text{K}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ superconductors.

x	Volume fraction of phases formed (%)	
	Bi-2223 phase	Bi-2212 phase
0.0	80.93	19.06
0.1	63.97	36.02
0.2	59.30	37.23
0.3	57.08	39.36
0.4	69.08	27.90
0.5	64.66	31.47

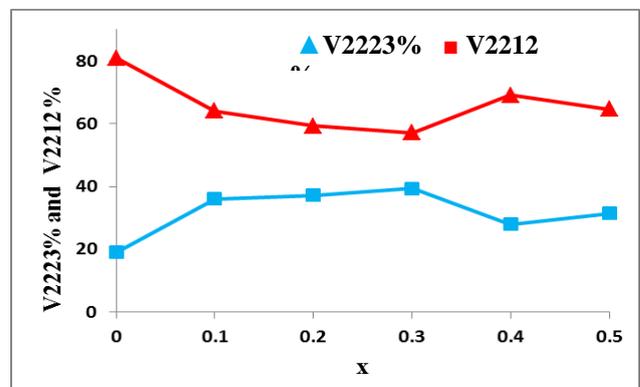


Figure 2: The volume fraction of Bi-(2223) and Bi-(2212) phases as function of K concentration for $\text{Bi}_{2-x}\text{K}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ superconductors.

The parameters a,b,c and V which calculated from the XRD analysis are listed in Table 2. It can be observed a random variation in both of a and c lattice constants with the substitution of K. In general, the substitutions up to 0.3 caused decreasing the c parameter whereas beyond it a remarkable increasing noticed. The increase in lattice parameter c revealed that cations of the, Sr^{2+} , Ca^{2+} in addition to Bi^{3+} may partly be substituted by K^{+1} ions ; similar behavior has been noticed by Yilmazlar[15].



Table 2: The parameters a,b,c , V and T_C for Bi_{2-x}K_xPb_{0.3}Sr₂Ca₂Cu₃O_{10+δ} superconductors.

x	a(Å)	b(Å)	c(Å)	V(Å) ³	T _C (K)
0.0	5.415875	5.45192	37.7274	1113.97382	115
0.1	5.407009	5.345372	37.21568	1075.62524	104.5
0.2	5.352627	5.543059	37.35088	1108.19789	105
0.3	5.441305	5.440183	37.07722	1097.54856	109
0.4	5.421206	5.423298	37.26304	1095.56377	115
0.5	5.370065	5.46913	37.48752	1100.99285	128

Measurements of electrical resistivity samples versus temperature with various amounts of K are displayed in figure 3. All samples reveal a metallic behavior in the normal state and a superconducting transition to zero resistance with T_C (115, 104.5, 105, 109, 115 and 128) K for (x=0, 01, 0.2, 0.3, 0.4, and 0.5) respectively. A broadening transition is observed and this may be due to the presence of impurities or non-superconducting regions or multi superconducting phases in the sample. The reduction of the critical temperature could be attributed to either crack formation as a result of excessive mechanical deformation, or to amorphous phase formation during the sintering process. In general T_C value increased with increasing K concentration this is mainly due to the strong link and increasing of the contact areas between the grains during the sintering process. It is well established that there are two types of superconducting grains, one formed by the 2223 phase and the second by the 2212 phase coupled together via some weak links and by passes the islands of the 2212 phase[16]. Once the volume fraction of 2223 phase within the sample is sufficient to make this possible, a one –step resistivity transition is observed even in the samples which contain a rather large amount of the 2221 phase. Samples with x=0.3 and 0.2 show two steps, reflecting the decrease of the intergrain transition. It is possible that the both superconducting phases exist within one grain in such a way that the low-T_C phase forms on the surface of the high-T_C phase one. In this case a sufficiently thin layer of the low –T_C phase can play a role in the weak link. This could mainly due to the strong link and increasing the contact areas between the grains during the sintering process in other words decrease of porosity [17]. The deformation in the c-axis adjusts the amount of charge transfer from Bi-O layer to Cu-O layer sheet will tend to improve the critical temperature. This behavior may be explained by the attribution to the differences in the ionic radii for both of K and Bi, which results in the c-axis elongation, then heightening of the high-T_C phase. A point of interest is that the highest transport mechanism is at x=0.5. This means higher resonant tunneling occurs between CuO₂ layers through localized centers across the c- parameter. Such result obtained by Thabit [18] for Bi-2223 superconductor substituted with higher Ni concentration. The deformation of the structure is always considered as the cause of the high conduction in the perovskite multi-layer state which gives rise to some kind of polarization at enough high T_C. This polarization will let the holes or electrons move long distance without suffering scattering process.

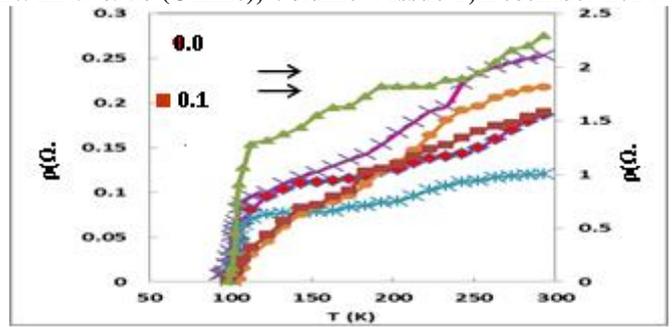


Figure 3: Temperature dependence of resistivity for Bi_{2-x}K_xPb_{0.3}Sr₂Ca₂Cu₃O_{10+δ} superconductors with 0 ≤ x ≤ 0.5 .

IV. CONCLUSION

Solid-state reaction method used to prepare Bi_{2-x}K_xPb_{0.3}Sr₂Ca₂Cu₃O_{10+δ} superconductors with 0 ≤ x ≤ 0.5. XRD results showed that all samples are polycrystalline and both (Bi,Pb) -2223 and -2212 phases coexist in the samples having orthorhombic crystal structure. It had been shown the substitution with K in combination with Pb promotes formation of high-T_C phase 2223. On other hand substitution of K and Pb altered the electronic structure of BSCCO system and simultaneously influences the superconducting T_C. The most important improvement in T_C; 128K was obtained by utilizing the nominal content of x = 0.5.

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