Cobalt substitution effect on the physical properties of (Bi, Pb)-2223 superconductor

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Abstract. High-temperature superconductors with a nominal composition Bi₂Pb₀.₃Sr₂Ca₂Cu₃₋ₓCoₓO₁₀₊δ for (0≤x≤3) were prepared by solid-state reaction method. Effects of the Co substitution on Cu sites have been investigated to obtain the optimum concentration for the formation and stabilization of the superconducting samples. The results of electrical resistivity measurements of the samples showed that increasing x substituting Co enhance the superconducting properties except for the samples with x= 3 yield semiconductor behavior. The higher critical temperature TₓC found at 118 K, which is for the composition Bi₂Pb₀.₃Sr₂Ca₂Cu₂.₂Co₀.₈O₁₀₊δ, which has the highest value of excess oxygen content 0.315. The X-ray diffraction analysis for all superconducting samples showed an orthorhombic structure with two phases, high-TₓC 2223 phase and low-TₓC 2212 phase. X-ray spectroscopy analysis showed that the compositions with x=0.6 and 0.8 samples did not contaminate during the synthesis processes. The scanning electron microscope has been used to identify the morphology of the superconducting phase. The plate-like grains of the high Bi- 2223 phase appeared in most micrographs of the superconducting samples besides changes morphology of samples with increasing dopant concentration.

Keywords: Superconductors; Cobalt; Substitution; Physical properties.

1. Introduction
Superconductor is a material that loses all resistivity due to the flow of electric current when it cooled below a certain temperature, which is called the critical temperature or transition temperature (TₓC).
Above this temperature, there is usually little or no indication that the material might be a superconductor [1]. BiSrCaCuO (BSCO) was the first high-temperature superconductor which does not contain any rare earth metals. This family of superconductors can be expressed by the general formula Bi$_2$Sr$_{2n-1}$Ca$_n$Cu$_{2n+4}$O$_{2n+4+\delta}$, where (n=1, 2, 3), the CuO layers, depend on n values. The Bi-2201, Bi-2212, and Bi-2223 phases have single, double, and triple layers of CuO$_2$ in the subunit cell, respectively. All three phases have in common both the conduction layer and the charge reservoir layer. The critical temperature of these materials increases with increasing the number of Cu-O planes in the crystalline structure [2, 3]. T$_c$ and lattice parameters of three systems change slightly depending on the cationic substitution, which occurs widely in any of these phases [4]. The T$_c$ between superconductive and nonsuperconductive states strongly depends on the concentration of carriers in the CuO$_2$ planes, which closely relates to structures in charge reservoirs and the number of CuO$_2$ planes [5].

Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_3$Ga$_{0.6}$O$_{6}$ was prepared with different concentration of Ge by solid-state reaction method [6]. It was shown that all the samples consist of both low-T$_c$ 2212 and high-T$_c$ 2223 phases. The percentage of low-2212 phase was found to increase with the increase Ga-content. Zero resistivity temperature T$_c$ was obtained to be less than 106 K for doped samples. The effects of Ti substitution on the properties of Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{1-y}$Ti$_y$O$_{10+\delta}$ bulk samples were studied for (0 ≤y ≤0.4). [7]. XRD analysis showed an orthorhombic structure with two phases high -2223 phase and Low -2212 phase, in addition, an impure phase was found. The highest critical temperature118 K was found for Bi$_{1.7}$Pb$_{0.3}$Sr$_3$Ca$_3$Cu$_3$Ti$_3$O$_{10+\delta}$ compound. This work was performed to improve the high 2223-phase formation and T$_c$ of BiPbSrCaCuO compound by partial substitution of Co in Cu sites. In addition, to clarify the common features of the substitution effect and as there is no report of Co substitution at least to our knowledge.

2. Experimental

The system of Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3.8}$Co$_{0.2}$O$_{10+\delta}$ with( x=0, 0.2, 0.4, 0.6, 0.8, 1, 2, 3) was prepared by a solid-state reaction method by mixing oxides, carbonates and nitrates Bi$_2$(CO$_3$)$_3$, PbO$_4$, Sr(NO$_3$)$_2$, CaCO$_3$, CuO and CoO with molecular weights equivalent to the proportion of high purity powders (99.9%). To get a homogeneous mixture, the powders were mixed using a gate mortar, a sufficient quantity of 2-propanol was added to form a paste during the process of grinding for about 1 h. Then the mixture was calcinated in the air at 800℃ for 24 h, and after that, the mixture was pressed into pellets (13mm) in diameter and(1.5) mm thick, using hydraulic type SPECAC, under pressure of 0.7 GPa. The pellets were sintered in air at 830℃, for 140 h. The structure of the prepared samples was obtained by using X-ray diffraction (XRD) Philips with CuKα source. The four-point probe method was used to measure the resistivity and to determine the T$_c$. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) type FEI-SEM model Inspect-S50 were used to study the surface morphology and analysis the composition of the samples.

3. Results and discussion

EDX spectra of the Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{2.4}$Co$_{0.5}$O$_{10+\delta}$ and Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_3$Cu$_2$Co$_{0.8}$O$_{10+\delta}$, superconductors are illustrated in Figures 1 and 2, which show that there is no unwanted element in the sample and implies that the samples are not contaminated during the synthesis process. Moreover, there is no change in the position of Bi, Pb, Sr, Ca, and Cu peaks. In comparison between the two samples, beside of the Co peaks at 0.7 KeV and 6.9 KeV for x=0.6 another peak that belongs to Co appeared at 0.9 KeV and 6.6 KeV for x=0.8. Overlap of some peaks such as Bi and Pb peaks at the same value of energy was observed indicating that Bi ions have partially replaced by Pb ions in the system. Moreover, overlapping is also noticed for Cu and Co. The results confirm that the desired elements in the chemical composition of the synthesized samples are present and well substituted.
Figure 1. The EDX analysis for Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{2.4}$Co$_{0.6}$O$_{10-δ}$ superconductor

Figure 2. The EDX analysis for Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{2.2}$Co$_{0.8}$O$_{10-δ}$ superconductor

XRD patterns of the nominal composition of Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_3$-xCo$_x$O$_{10+δ}$ for (0≤x≤3) sintered at 830 °C for 140h are shown in Figure 3. Peaks belong to high and low phases coexistence in the samples; but most of them belong to (Bi, Pb)-2223 phase. Some impurities phases like Sr$_2$Ca$_2$Cu$_7$O$_{δ}$ were detected at 2θ around 36° and the other is unknown. Some peaks belong to high T$_C$-2223 have intensity higher than those of the low-T$_C$ 2212 phase; this case appears more clearly with increasing Co content, and it indicates the increase of the crystalline arrangement degree [8]. Further increase of x=1-3 decreased the intensity most of the peaks yielded smaller grains (smaller crystallinities) as it will be seen in SEM results.

The relative volume fractions of the high Bi-2223 phase (V$_{2223}$) and low Bi-2212 phase (V$_{2212}$) were estimated using formulas in reference [9]. It can be observed in Table 1 and Figure 4 that Co concentration at 0.8 has the highest volume fraction of the Bi-2223 phase, which indicates that Co may act as a phase stabilizer and enhance the nucleation and the formation of high –T$_C$ phase. Further increase of x =1-3 changes the reaction rate and slows down (Bi, Pb)-2223 formation.
Figure 3. XRD patterns for Bi$_3$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ samples for $x=0$, 0.2, 0.4, 0.6, 0.8, 1 and 2 that sintered at 830 °C for 140 h.
The values of the lattice parameters a, b, c, unit cell volumes V, c/a ratio, and density $\rho_m$ of all the samples were calculated and summarized in Table 1. The density of the unit cell for all samples was calculated using the equation in reference [9]. The variation of both $\rho_m$ and c/a ratio as a function of Co content of Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ are shown in Figure 5. It can be obtained that there is an increase in both c lattice constant and c/a ratio with the increase of Co content (0<x<1). The reason is due to the differences of the ionic radii for both of Cu$^{+3}$(0.69Å) and Co$^{+2}$(0.78Å), which renders c-parameter to be longer or to get deformed. Such results may also be due to the distribution of holes between BiO 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]. On the other side, the gradual decrease of c parameter with increase Co concentration to 1, 2 and 3 decreases this ratio, which may be attributed to the charge ordering phenomenon induced by Co as well as to the change of the oxygen content. Moreover, the interaction between additional bands crosses the Fermi level to grab the holes from CuO band thereafter decrease of the distance between CuO$_2$ planes that perform the decrease of the c-axis taking into consideration replacement of Bi$^{+3}$ by Pb$^{+2}$ ions this agreement with Muna et al. results [11]. The change in a, b, c affects the volume of the unit cell, and so causes a change of density. An increase of the density could be explained by a reduction of the porosity and voids in the sample.
Table 1. Values of lattice parameters a, b, c, V, c/a ratio, volume fraction, and density for different composition of Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-\delta}$Co$_{\delta}$O$_{10+\delta}$.

| x   | a (Å) | b (Å) | c (Å) | c/a | V (Å$^3$) | $\rho_m$ (gm/cm$^3$) | V2223% | V2212% |
|------|-------|-------|-------|------|-----------|----------------------|--------|--------|
| 0    | 5.365 | 5.454 | 37.212| 6.936| 1088      | 1.436                | 79.554 | 19.556 |
| 0.2  | 5.447 | 5.361 | 37.149| 6.820| 1084      | 1.452                | 51.723 | 47.387 |
| 0.4  | 5.454 | 5.465 | 37.267| 6.832| 1110      | 1.456                | 68.934 | 30.176 |
| 0.6  | 5.447 | 5.456 | 37.297| 6.847| 1108      | 1.463                | 71.632 | 27.478 |
| 0.8  | 5.456 | 5.426 | 37.354| 6.846| 1105      | 1.483                | 77.762 | 21.348 |
| 1    | 5.449 | 5.562 | 37.112| 6.810| 1124      | 1.476                | 65.578 | 33.532 |
| 2    | 5.449 | 5.456 | 37.086| 6.806| 1102      | 1.592                | 53.712 | 45.398 |

Figures 6 and 7 show the resistivity as a function of temperature for Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-\delta}$Co$_{\delta}$O$_{10+\delta}$ with x ranging from 0 to 3 sintered at 830°C for 140h. All samples are superconductors except the composition with x=3, which is exhibited like semiconductor resistivity. Samples with x=1-2 showed linear behavior in the normal state, which indicates that these samples have optimally doped carriers in the CuO$_2$ plane, similar results were mentioned by Gul et al. [12]. A sharp drop of resistivity was observed for concentration s 0.6, 1 and 2 this reveals that the sample consists homogeneity of predominantly Bi-2223 phase [13, 14].

![Figure 6. Temperature dependence of resistivity for Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-\delta}$Co$_{\delta}$O$_{10+\delta}$ with x=0, 0.2, 0.4, 0.6 and 0.8.](image-url)
It can be noticed from Table 2 that the values of the transition temperature increase from 112K of pure sample to 113,114,117 and 118K depending on the doping concentration 0.2, 0.4, 0.6 and 0.8 respectively. While increasing Co content to x=1 and 2 decreases the transition temperature to 108 and 106K, respectively. Samples with x= 3 yield semiconductor behavior. These values indicate that increasing amounts of Co content causes stabilization and promotes the growth of the Bi$_2$-2212 phase at the expense of the Bi$_2$-2223 phase [15]. While increasing Co could distort the crystal structure by the extra oxygen intercalated between two adjacent BiO layers which then affected the hole concentration of the copper oxide planes after that decreases $T_C$ this result agrees with that obtained by Man et al. [16].

Table 2. Values of $T_C$ and oxygen content for nominal composition Bi$_2$ Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ with 0≤x≤3

| x  | $T_C$(K) | $\delta$    |
|----|----------|-------------|
| 0  | 112      | 0.2347      |
| 0.2| 113      | 0.2434      |
| 0.4| 114      | 0.2863      |
| 0.6| 117      | 0.2929      |
| 0.8| 118      | 0.31519     |
| 1  | 108      | 0.1592      |
| 2  | 106      | 0.1011      |
| 3  | Semi.    | -           |

Upon the results above, it is clear that the relation between $T_C$ and Co concentration is almost bell-like shape, as shown in Figure 8. The superconducting phase may be divided, such as the underdoped, optimally doped, and overdoped regions [17,18]. Most of the samples with the majority of Bi$_2$-2223 are in the underdoped state; their superconducting properties tend to optimal values with increasing Co content. Highest $T_C$ was determined at 0.8, which affirms that the sample is in an optimal doping region while a decrease of $T_C$ beyond this concentration appears to be due to the shift of this sample towards the over-doped region. Though increasing Co concentration decreases the $T_C$, it does not
suppress the formation of (BiPb)-2223 phase, which confirmed by XRD analysis. Similar behavior found by Muna et al. [19].

Table 2 and Figure 8 show the excess of oxygen content ($\delta$) for the samples $\text{Bi}_2\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ with $(0\leq x\leq 3)$. Both the $\delta$ and $T_C$ increased, with increasing $x$ to 0.8 and then reduced for further increasing of substitution, and there is a direct relationship between $O$ content and $T_C$ the higher value is found for a higher value of oxygen content as shown for the sample with $x=0.8$. This could be attributed to the increase in oxygen absorption during the crystallization process of the superconductors [20]. Thus excess oxygen atoms in the Cu-O$_2$ layers will create more holes in the perovskite layers, the creation of holes will shorten the Cu-O$_2$ bond length, and this leads to an improvement of the superconductor properties [21]. Increasing Co beyond 0.8, caused decrease both $\delta$ and $T_C$, this may be accompanied by changes in oxygen content or oxygen order effects which decrease the number of holes in the lattice from the optimum value [22]. Results suggest that as the hole concentration of the compound increases above a critical value, the superconductor is suppressed. Similar behavior which was emphasized by other researchers [19,23]. Furthermore, the addition of Pb to the compounds may relax the modulation by influencing the charge balance, oxygen content, and structural of the relevant layers [24].

Images of scanning electron micrographs of $\text{Bi}_2\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples are shown in Figures (9 - 15). All the $\text{Bi}_2\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples consisting of packets of plate-like shape and voids expect $x=1$ and 2. The surface area images of $\text{Bi}_2\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ show denser microstructure with some porous and irregular sizes of a stack of plate-like (agglomeration of grains) structure which belongs to the high-$T_C$ phase. Samples with $x=0.2$ show a composed structure of two kinds of particle features namely flaky grains clump of whisker which may be attributed to the cobalt addition (the flaky grains here more obvious) and the different size of stack irregular plate-like grains. This coalescence means the growth of the superconducting phase on account of its surrounding phase. Increasing Co concentration to 0.4, 0.6, and 0.8 cause the growth of the grain in a random direction through the other gain and creates bigger grains. That is in agreement with the results obtained by XRD also decreases the size of voids which enhances the junction between the grains and the formation of high-2223 phase, Which improves the superconducting properties of the samples and raising the $T_C$ values. On other side, Figures 14 and 15 illustrate how the surface of the samples become smoother, and the plate-like structure is destroyed. In other words, it shows very small size grains, indicating the poor formation of the superconducting phase.
4. Conclusions
The XRD and electrical resistivity results of BPSCCO samples indicate that the variation in lattice parameters and superconductivity behavior are mainly due to the structural distortion and charge ordering phenomenon, which induced by Co substitution in combination with Pb addition, promote the 2223 phase of samples. The maximum $T_c = 118$ K obtained at the concentration 0.8 in optimal doping regime. The improvement of the superconducting properties of samples is due to the better crystallinity, larger grains, and oxygen incorporation into the sample, which leads to the prominent

Figure 9. SEM micrographs of the fracture surface of the sample with two magnification and $x = 0.1$.

Figure 10. SEM micrographs of the fracture surface of the sample with two magnification and $x = 0.2$.

Figure 11. SEM micrographs of the fracture surface of the sample with two magnification and $x = 0.4$.

Figure 12. SEM micrographs of the fracture surface of the sample with two magnification and $x = 0.6$.

Figure 13. SEM micrographs of the fracture surface of the sample with two magnification and $x = 0.8$.

Figure 14. SEM micrographs of the fracture surface of the sample with two magnification and $x = 2$.

Figure 15. SEM micrographs of the fracture surface of the sample with two magnification and $x = 3$. 
enhancement of Tc. SEM micrographs show changes morphology of the material with an increasing dopant concentration.

References

[1] Fossheim K and Sudbo A 2005 *Superconductivity – Physics and Applications* John Willey and Sons Ltd.

[2] Agarwala P, Srivastava M P, Dheer P N, Pandmanaban P N and Gupat A K 1999 *Physica C* **313** 87

[3] Che G C, Du Y K and Zhao Z X 1994 *Solid-State Commun.* **89** 903.

[4] Hong Z, wang M, Xiong G, and Fan X 1997 *Physica C* **288** 82.

[5] Khan M N and Zakaullah Kh 2006 J. Rese. Sci. **17** 59.

[6] Muhammad I and Mahmood R 2012 World Appl. Sci. J. **17** 1510.

[7] Hermiz G Y, Jassim A K, Alwan E K 2015 Asian Academic Rese. J. Multidisciplinary **2** 281.

[8] Abbas M M, Abbas L K and Salman U 2012 Energy Procedia **18** 215.

[9] Bilgili O, Selamet Y and Kocabas K 2008 J. Super. and Novel Magn. **21** 439.

[10] AL-Dahash A G 1998 *Effect of Deformation on Electronic Structure and Magnetic Properties of Some High-Temperature Superconductors* Ph.D. Thesis Baghdad University.

[11] Abbas M M, Abdulridha A, Jassim A J, and Hashim F 2018 Citation: AIP Conference Proceedings 030009.

[12] Gul I H, Rehman M A, Ali M and Maqsood A 2005 **432** 71.

[13] Iqbal M J, Mehmoon R 2009 *J. Alloys and Compound* **477** 386.

[14] Hermiz G Y, Muna M A and Gilioli E 2009, Attidela Fodazione Giorgio Ronchi Anno Lxiv **2** 313.

[15] Awad R J 2012 J. Supercon.and Novel Magnet. **25** 739.

[16] Man N K, Garg K B, Hien T D, Sinh N H, Phuc N X and enkatesh S V 1998 J. Magnetism and Magnetic Materials **527** 177.

[17] Fuji T, Terasaki I, Watanabe T and Matsuda A 2002 *Phys. Rev. B* **66**

[18] Parinov I A 2012 *Microstructure and Properties of High-Temperature Superconductors* Springer-Verlag Berlin.

[19] Abbas M M, Oboudi S F and Raooof N Q 2015 *Materials Scie. and Applica.* **6** 310.

[20] Giri R, Singh H K, Tiwari R S and Srivastava O N 2001 *Bull. Mater. Sci.* **24** 523.

[21] Hermiz G Y 2001 *Thermal Analysis and phase transformation of HTSC of (Bi1-xPb)x2(Sr1-yBa,y)2Ca2Cu3O10 compound* Ph.D. Baghdad University.

[22] Salamati H, Morshedloo T, Kameli P, Baghi M, Abdolhosseini I, Ahmadvand H and Sohrabi D 2010 *Iranian J. Phy. Rese., Proceedings of the Second National Conference on Advances in Superconductivity*, **10** 2.

[23] Abbas M M, Abbas L K and Bahedh H S 2015 J. Applied Sci. Rese. **11** 164.

[24] Ikeda Y, Takno M, Hiroi Z, Oda K, Kitaguchi H, Takada J, Miura Y, Takada Y, Yamamoto O, and Mazaki H 1988 *Jap. J.Appl.Phys* **27** 2067.