Effect of sintering temperature on superconducting properties of Bi$_2$Pb$_{2-x}$Sr$_2$Ca$_2$Cu$_3$Co$_x$O$_{10+\delta}$ system

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Abstract. Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ high temperature superconductors with $x=0, 0.2$ and $0.4$ were prepared by a solid state reaction method. The samples properties have been investigated structurally by X-ray diffraction and morphologically by scanning electron microscopy. Structural analysis showed that two superconducting phases coexist in the samples high temperature Bi-2223 and low-temperature phase 2212 with orthorhombic structure for all samples. Four point probe method was used to study the electrical properties of the samples and all of them showed superconductivity behavior. The transition temperature increases with the increasing Co concentration and sintering temperature. Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ superconductor sintered at 1300°C shows highest critical temperature 114 K.

1. Introduction

High temperature superconductors, BiSrCaCuO compounds were discovered in 1988 [1]. They have three different phases a Bi-2201 phase, a Bi-2212 phase, and a Bi-2223 phase, according to their compositions; each phase has a different transition temperature to the superconducting state [2,3]. The Bi-2223 phase attracted greater interest due to its high critical temperature.

The grain connectivity and the degree of texturing in the Bi-2223 compound depends on various parameters such as starting composition, sintering time and temperature [4]. Azhan et al. showed that the heat treatments at 830°C and 860°C; increases the critical temperature of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ system [5]. Muna et al. pointed out that increasing of sintering temperature promotes the formation of high- critical temperature (T$_C$) phase 2223 due to improvement of the nucleation [6]. Ghazala et al. studied the effect of sintering temperature on BPSCCO Superconductor system prepared by solid state reaction method. The result indicated that there is a decomposition of the high-T$_C$ phase with the increasing of the sintering temperature [7].

On other hand, the superconducting properties can be modified by the addition or substitution of an element with a different ionic radius and bonding characteristics. In addition the existence of Pb in the started materials promotes the reaction kinetics of the Bi- (2223) phase and enhances the diffusion of the calcium and copper atoms [8]. Jannah et al. studied the effect of nano Co$_3$O$_4$ addition on the properties of BPCCO system prepared by solid state reaction method. They showed that appropriate amount of Co enhanced the critical temperature of Bi(Pb)SrCaCuO superconductor and the samples have both high-TC phase 2223 and low-T$_C$ phase 2212 [9].
The aim of this work is to prepare and investigate the properties of Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ superconductors with the different sintering temperature and Co concentration.

2. Experimental

Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ samples with x=0, 0.2 and 0.4 were prepared by a solid state reaction method. Appropriate weight of high purity powders of materials Bi$_2$(CO$_3$)$_3$, PbO$_4$, Sr(NO$_3$)$_2$, CaCo$_3$, CuO and CoO were mixed. The mixture was calcined in air at 800 ºC for 24 h. Then the powders pressed into disk-shaped pellets under pressure 0.5 GPa using hydraulic press type (Specac). The pellets were sintered in air at sintering temperature (Ts) (820, 830, 835 and 840) ºC for 140 h.

The electrical resistivity ($\rho$) of the samples as a function of temperature were obtained by using four point probe DC method at temperature range (77 - 300) K to determine the critical temperature (Tc). The crystal structure of the prepared samples was obtained by using X-ray diffractometer type Philips Source: CuK$\alpha$ radiation. The lattice parameters were calculated by using a computer program based on Cohen's least square method [3]. The oxygen content ($\delta$) in the superconductor samples was determined by using iodometric titration technique.

Scanning electron microscopy (SEM) type FEI-SEM model Inspect –S50 were used to study the surface topography of the samples.

3. Results and discussion

XRD patterns of Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ system for different values of x sintered at 820 and 830ºC are shown in Figs.(1-3). The spectra shows an orthorhombic structure of all samples and most of them have two phases Bi-2223 and Bi-2212, in addition these of phases there were some unknown and impurity phase like Sr$_2$Ca$_2$Cu$_7$O$_{\delta}$ is detected at $2\theta$ ≈ 36.8º as reported by Asthana [10]. The appearance of more than two phases could be related to the stacking faults along the c- axis as a result of the displacement of an ion or oxygen defect or to the ordering of cations [11,12].

It could be seen that increase the sintering temperature causes an increase the intensity of the peaks. The most intense peak pattern of samples belongs to the high-2223 phase which also indicates an increase in the volume fraction of this phase [13]. Another feature observed is a present of H(0012) for all samples which is necessary to prove the superconductivity for Bi-compound.

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 [14].

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. Density of unit cell for all samples was calculated using the following equation in reference [15].
Figure 1. XRD patterns for Bi$_{2}$Pb$_{0.3}$Sr$_{2}$Ca$_{2}$Cu$_{3}$O$_{10+\delta}$ sintered at 820 °C and 830 °C for 140h.

Figure 2. XRD patterns for Bi$_{2}$Pb$_{0.3}$Sr$_{2}$Ca$_{2}$Cu$_{2.8}$Co$_{0.2}$O$_{10+\delta}$ sintered at 820 °C and 830 °C for 140h.
Figure 3. XRD patterns for Bi$_2$Pb$_{0.3}$Sr$_2$Cu$_{2.8}$Co$_{0.4}$O$_{10+\delta}$ sintered at 820ºC and 830ºC for 140h.

Table 1. Values of lattice parameters, unit cell volume, c/a ratio, $V_{2223}$, $V_{2212}$ and density $\rho_m$ for all samples.

| Ts (ºC) | x  | a (Å) | b (Å) | c (Å) | $V(Å)^3$ | c/a | $\rho_m$ (gm/cm$^3$) | $V_{2223}$ % | $V_{2212}$ % |
|---------|----|-------|-------|-------|----------|-----|-----------------|-------------|-------------|
| 820     | 0  | 5.403 | 5.477 | 37.007| 1095     | 6.849| 1.428           | 69.632      | 29.478      |
|         | 0.2| 5.406 | 5.322 | 36.671| 1055     | 6.783| 1.507           | 41.543      | 57.567      |
|         | 0.4| 5.403 | 5.352 | 36.846| 1065     | 6.819| 1.503           | 68.854      | 30.256      |
| 830     | 0  | 5.365 | 5.454 | 37.212| 1088     | 6.936| 1.436           | 79.554      | 19.556      |
|         | 0.2| 5.447 | 5.361 | 37.149| 1084     | 6.820| 1.452           | 51.723      | 47.387      |
|         | 0.4| 5.454 | 5.465 | 37.267| 1110     | 6.832| 1.456           | 68.934      | 30.176      |

Measurements of electrical resistivity as a function of temperature showed metallic behavior of the samples as displayed in Figs (4, 5 and 6) respectively. Superconducting transitions to zero resistance had been noticed for the samples sintered at 830 ºC. While a complete zero resistance was not observed for the samples sintered at 820 ºC. This could be due to the transition within the grains and the presence of Bi-2221 phase [11].

From Table (1) and the see that the transition temperature of the compositions Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$, Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_{2.8}$Cu$_{2.6}$Co$_{0.2}$O$_{10+\delta}$ and Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{2.8}$Co$_{0.4}$O$_{10+\delta}$ increases from 103, 101 and 108K to 112, 113 and 114K respectively as the sintering temperature increasing from 820 C to 830C.

Enhancement of Tc with increasing Co could mainly due to increasing amounts of Bi-2223 phase as referred in the x-ray analysis, as well as to the increasing the contact areas between the grains which improved the junctions between them during the sintering process with increasing sintering temperature [16 and 17].
Sintering at temperatures 835°C and 840°C produced melted and bended samples; therefore, the sintering temperature is considered critical for the growth of high-\(T_c\) phase and the optimum temperature seems to be close to the partial melting point, this agreement with Ghazala et al. [7].

![Figure 4](image1.png)

**Figure 4.** Temperature dependence of resistivity for Bi\(_2\)Pb\(_{0.3}\)Sr\(_2\)Ca\(_3\)Cu\(_3\)\(O_{10+\delta}\) sintered at 820°C and 830°C for 140h.

![Figure 5](image2.png)

**Figure 5.** Temperature dependence of resistivity for Bi\(_2\)Pb\(_{0.3}\)Sr\(_2\)Ca\(_2\)Cu\(_{2.8}\)Co\(_{0.2}\)\(O_{10+\delta}\) sintered at 820°C and 830°C for 140h.
The oxidation of Bi-2223 superconductor refers to sintering conditions which can occur within the nucleation, growth and reaction process. Bi-2223 compound is very sensitive to oxygen. It can be inferred from Table 2 that both the $\delta$ and $T_C$ increase with increasing Co concentration and sintering temperature. The higher $T_C$ value is found for higher value of oxygen content for the samples sintered at 830°C. This could be attributed to the increase of oxygen absorption during crystallization process of the superconductors and this leads to an improvement of the $T_C$ [18].

**Table 2. Values of the oxygen content and critical temperature for all samples.**

| $x$ | $T_s$ (°C) | Oxygen contact ($\delta$) | $T_C$ (K) |
|-----|------------|---------------------------|-----------|
| 0   | 820        | 0.0984                    | 103       |
| 0.2 | 820        | 0.0965                    | 101       |
| 0.4 | 820        | 0.0932                    | 108       |
| 0   | 830        | 0.2347                    | 112       |
| 0.2 | 830        | 0.2434                    | 113       |
| 0.4 | 830        | 0.2863                    | 114       |

Surface topography morphology of the samples with $x=0.4$ sintered at 820°C and 830°C illustrates in Fig. (7). The images show a composed of different size of stacks irregular plate-like grains.

**Figure 6.** Temperature dependence of resistivity for Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{2.8}$Co$_{0.4}$O$_{10+\delta}$ sintered at 820°C and 830°C for 140h.
increasing the sintering temperature leads to form a large grains and enhance the formation of high- $T_C$ phase, each grain grows in random direction through the other gain and creates bigger grains. This coalescence between the grains reveals the growth of the superconducting phase on the account its surrounding phase. However, the enhancement of the samples behavior could be attributed to decreasing the porosity and increasing the contact between the grains during the sintering process time. This confirms our explanation of the higher $T_C$.

Figure 7. SEM micrographs of fracture surface of samples with $x=0.4$ sintered at (a)820°C, (b)830°C.

4. Conclusions
The results showed that the properties of Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{3-x}$Co$_x$O$_{10+\delta}$ superconductors with $x=0$, 0.2 and 0.4 depend not only on element composition but it is also much delicate with the sintering process. The sintering temperature is critical for the growth of high- $T_C$ phase and the optimum temperature seems to be close to the partial melting point 830°C. The substitution Co in combination with increase the sintering temperature leads to form large grains and enhance the formation of high-temperature 2223-phase. Highest transition temperature has been determined 114 K for the composition Bi$_2$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_{2.6}$Co$_{0.4}$O$_{10+\delta}$ accompanied with higher value of oxygen content.

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