The effects of carbon nanotubes (CNT) on fabrication of Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire

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Abstract. This study aims to determine the effects of adding 0.1 %wt CNT on fabrication of Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire. The method used in this research is powder in tube (PIT). The PIT consists of several process stages; preparation of precursor, compaction of precursor in tube, wire rolling, and heat treatment. Powder mixing Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ and CNT using mortar agate for 3 hours. Rolling is done twice, up to 5 and 2.6 mm wire diameter. The heat treatment consists of the calcination at 820 °C for 20 hours and sintering at 850 °C with time variation of 9 and 30 hours. Characterization of superconductivity was performed by using cryogenic magnet to determine the critical temperature (Tc), SEM-EDX to analyze morphology, and XRD to discover the phase formed. From the research, it was found that the sample sintered for 30 hours with the diameter of 5 mm produced Tc$_{onset}$ = 109.17 K, with phase formed is Bi(Pb)$_{2212}$. While the samples sintered for 9 hours with a diameter of 5 mm produced Tc$_{onset}$ = 79.5 K, with phase Bi(Pb)$_{2212}$. Moreover, the addition of CNT reduced the value of grain size. But, sample with 2.6 mm in diameter didn’t show superconductivity properties.

1. Introduction
Superconductivity is an interesting phenomenon to be observed in some materials. This material loses its electrical resistance and rejects the magnetic field when cooled under the critical temperature (Tc) [1]. Superconductors were first discovered by Onnes in the early 1900s. Onnes investigated the electrical resistance of pure metals at low temperatures, i.e. mercury. He found that mercury resistance suddenly dropped to zero under 4 K temperature, this phenomenon he called superconductivity [2].

The ceramic superconductor that attracts the most attention of researchers is the Bi(Pb)-2223 superconductor, because it is a high-temperature superconductor. The use of Pb doping in the superconducting synthesis of the Bismuth system is due to the resemblance of the size of the ion and the valence of the Pb atom, resulting in the substitution of the Bi atom by the Pb atom in the BiO double layer [3]. Therefore, substitution of Pb helps stabilize the BSCCO-2223 superconductor at critical temperature (Tc) and also increases the volume fraction in phase 2223 [4].

Selection of sintering temperature for Bi-2201 phase formation ranges from 650-840 °C, while the 2212 and 2223 phases range from 840-890 °C with Ca$_2$CuO$_3$ and CuO impurities [3].
In recent years, doping such as CNT has increased the cuprate [5,6,7,8], since it is known to reduce grain size to increase critical current density (Jc) [9]. In addition, the CNT vacuum chamber itself has a high current density, even higher than metals and superconductors [10], which range from 109-1010 Ampere/cm² [11,12,13]. Several studies investigated the effect of adding CNTs focused on the superconducting phases of Y-123 and Bi (Pb)-2212 [5,7]. In another study, it was mentioned that the addition of CNT in BPSCCO was somewhat appropriate because the Tc obtained was quite high at 114.51 K, although the phase Bi(Pb)-2212 was indicated [14].

Along with its development, superconducting technology has reached the manufacture of monofilament wire and multifilament, one of which is in the manufacture of high temperature Bi-2223 superconductor wire enclosed by Ag using powder in tube (PIT) method [15]. The PIT method is mostly used because it is the simplest procedure. The procedure in this method consists of two types, namely (i) the powder is inserted in the tube and compacted in the tube manually, (ii) the powder is pressed isostatically and fed into a metal tube in precompacted form [16].

The manufacture of high temperature Bi-2223 superconductor wire enclosed by Ag using PIT method shows that Tc produced on multifilament wire manufacture has greater value than superconducting pellets and monofilament wire which is 119.5 K with 81 monofilament wire in a multifilament wire, although its multifilament diameter is smaller. However, the optimum temperature in the study was not obtained from the substitution of Pb on Bi, but the use of pure Bi(NO₃)₃, Sr(NO₃)₂, CaCO₃, and CuO [15]. From another study, Tc onset obtained a value of 96 K and Tc zero 64.4 K generated on the manufacture of wire Ag/Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₁₀ with sintering temperature 850°C (second sintering) for 30 hours [17].

This research was conducted with the aim to determine the effect of adding 0.1% wt CNT (carbon nanotube) on the manufacture of wire Ag/Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₁₀ using PIT method (powder in tube).

2. Method

The material used is powder Bismuth (II) Oxide (Bi₂O₃) with purity of 98%, Strontium Carbonate (SrCO₃) with purity 96%, Calcium Carbonate (CaCO₃) with purity 99% PA, Copper Oxide (CuO₂) with purity PA 99%, Lead Oxide (PbO₂) with PA purity 97%, CNT with purity of> 99% PA, Tube Ag.

The tools used in the manufacture of wire Ag/Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₁₀ with the addition of CNT in this study are digital scales, crusher (pastel and mortar Agate), heating furnace, pellet mold, crussible, press machine, rolling tool. While the equipments for testing in this research are Cryogenic Magnet type Teslatron Oxford Instruments, XRD type Rigaku Miniflex 600, and SEM EDS brand Zeiss & Jeol.

The first stage on fabrication of Ag/Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₁₀ wire with the addition of CNT is the preparation and weighing of Bi₂O₃, SrCO₃, CaCO₃, CuO₂, and PbO₂ with stoichiometric calculation of BPSCCO phase 2223. Then, CNT powder is added by 0.1 (wt%) of mass of BPSCCO powder phase 2223. Mixing of precursors was performed using mortar for 3 hours.

Before the powder was inserted into the Ag tube, The Ag tubes was solutionized to remove impurities. Cooling was performed using annealing method at 700 °C for 1 hour. Then, the powder Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₁₀ with the addition of 0.1% wt CNT is inserted into Ag tube which is 8 mm in diameter and has a length of 5 cm. Emphasis was done manually. Ag/Bi₁.₆Pb₀.₄Sr₂Ca₂Cu₃O₁₀ wire with the addition of prepared CNTS was then calcined at 820 °C for 20 hours. Then, the first rolling was done to alter the diameter, which has the initial value of 8 mm, to 5 mm.
Figure 1. Fabrication of Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire with the addition of CNT
Next, the wire was divided into two parts, the first part was sintered with temperature of 850 °C for 30 hours (labeled as A2) and the second part was done sintering with temperature of 850 °C for 9 hours (labeled as B2).

The Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire with the addition of CNTs sintered with the time variation was characterized using cryogenic to discover the Tc (critical temperature) obtained, SEM to analyze the morphology, and XRD to analyze the formed phase. The XRD measurement data were analyzed using Match v1.10 software in accordance with the 2003 International Center for Diffraction Data (ICDD) database and the volume fraction of XRD measurement results.

3. Result and Discussions

The results of Tc on the graph of resistivity and temperature relationship were obtained by the test using cryogenic magnet (Figure 2).

![Figure 2](image2.png)

Figure 2. Relation of resistance to temperature (a) sample A2 and (b) sample F2

From the graph of resistance and temperature relation shown in Figure 2, (a) it can be seen that for A2 sample obtained Tc$_{onset}$ = 109.17 K and Tc$_{zero}$ = 71 K. However, at the time of the second rolling to 2.6 mm diameter the wire is obtained Tc$_{onset}$ = 90 K, but Tc$_{zero}$ is not generated. This is shown in Figure 2, (b) with the graph tends to resemble the graph of resistance relationship and characteristic temperature of the conductor material. When compared to the manufacture of BPSCCO wire using Ag tube without adding CNT (without dopant) elements with Tc$_{onset}$ = 93K and Tc$_{zero}$ = 64 K [10], the addition of CNT causes an increase in the critical temperature (Tc).

For B2 and G2 sample, the graph of resistance and temperature relation shown in Figure 3.

![Figure 3](image3.png)

Figure 3. Relation of resistance to temperature (a) sample B2 and (b) sample G2
From the test shown in Figure 3, it can be seen that the obtained $T_{c\text{onset}}$ is 79.5 K and $T_{c\text{zero}}$ is 64.7 K. However, the sample G2 or sample of the second rolling, sintering for 9 hours (shown in Figure 3. (b)) yielded $T_{c\text{onset}} = 80$ K without generating $T_{c\text{zero}}$. It occurs due to the resulting graph tends to resemble the graph of resistance relationship and characteristic temperature of the conductor material. Critical temperature test results (Tc) using cryogenic magnets are also shown in Table 1.

| Sample Code | Diameter (mm) | Sintering T (°C) | t (h) | $T_{c\text{onset}}$ (K) | $T_{c\text{zero}}$ (K) |
|-------------|---------------|------------------|-------|-------------------------|------------------------|
| A2          | 5             | 850              | 30    | 109.17                  | 71                     |
| F2          | 2.6           | 850              | 30    | 90                      | -                      |
| B2          | 5             | 850              | 9     | 79.5                    | 64.7                   |
| G2          | 2.6           | 850              | 9     | 80                      | -                      |

XRD test results to identify the phase formed on wire fabrication Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ with the addition of CNT is shown in Figure 4.

![Figure 4. Diffraction Patterns of samples (a) A2 and (b) B2](image)

XRD phase analysis shows that both sample A2 and B2 identified phase Bi-2212. This is shown in the analysis of the formed phase and volume fraction. In Figure 4, (a) the formed phases are Bi(Pb)-2212, Bi(Pb)-2223, Ag, and 3 impurity phases, i.e. CuO, CaCO$_3$, and Ca$_2$PbO$_4$. Phase Bi(Pb)-2212 optimum at $2\theta = 23.15^\circ$ with intensity 7 cts, optimum phase Bi(Pb)-2223 at $2\theta = 59.15^\circ$ with intensity 6 cts, Ag phase at $2\theta = 44, 54^\circ$ with intensity of 12 cts; $2\theta = 64,69^\circ$ with intensity 8 cts; $2\theta = 77,68^\circ$ with intensity 23 cts; and $2\theta = 81,88^\circ$ with intensity 8 cts. CuO impurity phase is at 2 angle that is at $2\theta = 38,72^\circ$ with intensity 85 cts and $2\theta = 65,84^\circ$ with intensity 11 cts, CaCO$_3$ impurity phase is at 2 angle, i.e $2\theta = 43,11^\circ$ with intensity 49 cts and $2\theta = 48,46^\circ$ with intensity 6 cts, and Ca$_2$PbO$_4$ impurity phase is at $2\theta = 45,02^\circ$ with intensity 78 cts. These results indicate that the addition of CNTs in Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ increases the appearance of other impurities besides CuO, i.e. CaCO$_3$ and Ca$_2$PbO$_4$.

In the Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire sample with the addition of 0.1% wt CNT (labeled as B2) that is shown in Figure 4, (b), some phases are identified: phase Bi(Pb)-2212 that is optimum at $2\theta =$
31.1° and 20 = 56.75° with intensity 10 cts; phase Bi(Pb)-2223 at 2θ = 58.39° with intensity 12 cts; phase of sheathing Ag at 2θ = 45.21° with intensity 86 cts, at 2θ = 64.50° with intensity 13 cts, 2θ = 76.73° with intensity 10 cts, and 2θ = 82.26° with intensity 28 cts; CuO impurity phase at 3 angle, ie at 2θ = 38.72° with intensity 73 cts, at 2θ = 61.54° with intensity 6 cts, and at 2θ = 66.51° with intensity 21 cts; CaCO₃ impurity phase is at 3 angles, ie 2θ = 36.04° with intensity 5 cts, 2θ = 37.19° with intensity 24 cts, and 2θ = 48.46° with intensity 15 cts; and Ca₃PbO₄ impurity phase is at 2 angle, ie at 2θ = 30.60° with intensity 11 cts and at 2θ = 45° with intensity 79 cts.

When compared to the manufacture of BPSCCO wire using Ag tube without adding CNT or without dopant [10], the optimum phase formation Bi(Pb)-2212 at 2θ = 47.69° with the intensity of 22 count sec on (cts), phase Bi(Pb)-2223 optimum at 2θ = 28.78° with intensity 19 cts, by having fewer impurity phases, i.e. CuO impurity phase is at 4 angle, that is at 2θ = 3776° with intensity 169 cts, 2θ = 66.41° with intensity 9 cts, 2θ = 68.13° with instances of 12 cts, and 2θ = 75.01° with an intensity of 4 cts [15]. The CuO phase is an impurity phase in the sample Bi₁₆Pb₀₄Sr₂Ca₂Cu₃O₁₀ [2] formed by the decomposition of the Bi₂CuO₃ phase during the calcination process above 750 °C [18]. As a result of the formation of this impurities phase, the critical temperature of the sample was reduced [19].

The results from the above analysis prove that the addition of 0.1% wt of CNT adds impurity to the Bi₁₆Pb₀₄Sr₂Ca₂Cu₃O₁₀ system, this is indicated by the presence of an impurity phase other than CuO, in the addition of CNT in Bi₁₆Pb₀₄Sr₂Ca₂Cu₃O₁₀ system, ie CaCO₃ and Ca₃PbO₄. Both samples A2 and B2 produced the same identified phase: phases Bi(Pb)-2212. However, the difference between the two can be seen in the use of different sintering times, A2 sample results in a lower 2223 phase intensity than that of the B2 sample. The purity percentage of Bi(Pb)-2212 can be determined by computing the volume fraction ratio. The volume fraction and crystal size values of each sample are shown in Table 2.

| Sample Code | Volume Fraction (%) | Crystal Size (nm) |
|-------------|---------------------|-------------------|
|             | Bi(Pb)-2212         | Bi(Pb)-2223       |                  |
| A2          | 65.91               | 34.09             | 160.73           |
| B2          | 59.1                | 40.90             | 413.16           |

Table 2 shows that the ratio of volume Bi(Pb)-2212 and Bi(Pb)-2223 on sample A2 with 30 hours sintering time is 65.91% and 34.09%. While on sample B2 with time sintering 9 hour that is 59.1% and 40.90%. Based on the fraction of the volume, sintering for 30 hours on the Ag/Bi₁₆Pb₀₄Sr₂Ca₂Cu₃O₁₀ wire making with the addition of 0.1% wt CNT can decrease the phase 2223, on the contrary at 9 hours sintering time can raise phase 2223 even though the dominant phase is still in phase 2212.

The crystal size analysis shown in Table 2 also proves that the addition of CNTs into powder Bi₁₆Pb₀₄Sr₂Ca₂Cu₃O₁₀ can reduce the size of crystals, if compared to the manufacture of BPSCCO wire using Ag tube without adding CNT or without dopant with a grain size value = 546.22 nm [17]. The smallest crystalline size was obtained on the manufacture of Ag/ Bi₁₆Pb₀₄Sr₂Ca₂Cu₃O₁₀ wire with the addition of 0.1%wt, first sintered CNT (T = 850 °C for 30 hours), and 5 mm in diameter.

From the phase formed both on samples A2 and B2 obtained orthorhombic crystal structure with lattice parameter a = 5.347 Å, b = 5.416 Å, and c = 30.67 Å.
The morphology of Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire sample, which was obtained from SEM, was depicted in Figure 5. In Figure 5 (a) it appears that the size of A2 sample grain is smaller than the B2 sample. This is the evident from the grain size obtained in the XRD results analysis.

4. Conclusions

From the results of research on the effect of adding 0.1% wt of CNT on fabrication of Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire, it can be concluded that the addition of 0.1% wt of CNT on fabrication of Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire produce higher Tc (critical temperature) than that of Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ wire without CNT addition. Also, the addition of CNT can reduce the grain size. However, the addition of 0.1% wt of CNT on wire manufacture Ag/Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ causes the appearance of impurity phases, such as CuO, Ca$_2$PbO$_4$, and CaCO$_3$. The optimum critical temperature (Tc) produced, $Tc_{onset} = 109.17$ K and $Tc_{zero} = 71$ K, on the addition of 0.1% wt. CNT of the first sintering result at 850 °C for 30 h and the phase formed is phase Bi(Pb)-2212.

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