Effect of BaCO$_3$ addition on critical temperature of Bi-Pb-Sr-Ca-Cu-O superconductor

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Abstract: Bi-Pb-Sr-Ca-Cu-O high temperature superconductor has been applied in the field of electricity as power transport cables. This work has been carried out to investigate the effect of addition of BaCO$_3$ on Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_2$O$_{10}$superconductors. Solid state reaction method was used to prepare all samples. The starting materials were Bi$_2$O$_3$, PbO$_2$, SrCO$_3$, CaCO$_3$, CuO, and BaCO$_3$ powder. Starting materials without BaCO$_3$ were ground using a mortar agate for 3 h. After calcination process of 820°C for 20 h, samples were mixed with BaCO$_3$ (1 %wt, 2 %wt) and then sintered by 850°C for 30 h. Characterizations ware conducted by using cryogenic magnet to determine the critical temperature (Tc), SEM-EDX to analyze morphology, and XRD to determine the phase formed. There were semiconductor propertie at high temperature and it was found that the addition of BaCO$_3$ decreased Tc of the samples. 1 %wt BaCO$_3$ showed a critical temperature with $T_{c\text{onset}}$ = 86 K and $T_{c\text{zero}}$ = 52 K, and 2 %wt of BaCO$_3$ has $T_{c\text{onset}}$ of 80 K, and $T_{c\text{zero}}$ of 23 K. The surface morphology contains agglomeration and there is a lot of porosity. The dominant phase formed is Bi(Pb) - 2212 with a volume fraction of 64.71%.

1. Introduction

One particular material that holds promise for humans is a superconductor. It is a common in human life, to increase the economic growth usually it requires the availability of adequate and fast infrastructure. Examples of applications in this superconductor are power transmission cables, super high magnetic field generator in MRI (Magnetic Resonance Imaging), super-fast trains (Maglev Train) [18]. Superconductors are materials that have the characteristics of being able to conduct electric current without experiencing resistance, where the resistivity becomes zero and can repel external magnetic fluxes that pass through it or experience perfect diamagnetism (Meissner effect) [2]. One of the high temperature superconductors (HTS) is Bi-Sr-Ca-Cu-O (BSCCO). it has three superconductive phases, usually referred to as Bi-2201 (Tc ~ 10 K), Bi-2212 (Tc ~ 80 K), and Bi-2223 (Tc ~ 110 K) [11]. BSCCO is a ceramic oxide compound which has a multi-layered structure with a characteristic CuO$_2$ layer insertion [7]. There is a correlation between the superconducting structure and the critical temperature [6]. The most promising phase for this application is Bi-2223 because of the highest critical temperature (Tc) [17]. However, it is difficult to get single-phase 2223 because of its low stability [4]. The use of Pb doping in the superconducting synthesis of the bismuth system can facilitate the compounds with high phase purity levels. The addition of Pb as doping results in the substitution of Bi atoms by Pb atoms in the BiO double layer, because the Pb atoms have similar ion sizes and valences with Bi atoms [13].
Therefore Pb can stabilize the superconductor BSCO-2223, increase the critical temperature (Tc) and the phase volume fraction of 2223 [14].

One type of oxide compound is BaCO₃, it compound is considered capable of being doping to improve the grain density of BPSCCO because it has mechanical properties and a high melting point [10]. The composition of the initial elements used in Bi-2223 is very important with the addition of elemental Ba [15]. The appropriate amount of Ba when added to the BSCO superconductor has a large effect on the higher Tc and single phase transition [1]. The results of XRD and SEM analysis show that Ba doping up to x = 0.1 will increase the formation of Bi-2223 phase, and increase the superconductivity of the sample. However, the Tc value starts to appear lower for x > 0.1 [16]. The superconductivity and phase formation properties of Bi-2223 will decrease with increasing Ba concentration [15]. Ba substitution at both sites (Bi or Sr) lowers the sintering temperature for high Tc formation (small volume fraction). In Ba-doped BSCO there is a non-superconducting phase. The diffraction pattern formed is the dominant Bi-2212 phase. The effect of adding Ba on the BSCO system is very interesting to study, because they both belong to the same alkaline earth metal group and have different ionic radii [5]. Therefore, another way is needed to improve the mechanical properties of BPSCCO while increasing the critical temperature of the sample.

The solid state reaction method is a method that is widely used in the manufacture of superconductors, especially in high temperature superconductors (HTS) [8], such as bismuth (Bi) based superconductors [19] because the process is faster in the synthesis of superconducting materials, and the cost is relatively cheap [20]. In this research, a solid state reaction method was chosen to manufacture the superconducting BiₓPbₓSr₂Ca₂Cu₃O₁₀ with the addition of BaCO₃ doping. The research describes the effect of critical temperature (Tc) on the superconducting Bi-Pb-Sr-Ca-Cu-O.

2. Experimental
The BPSCCO sample used as the main material was made from a mixture of Bi₂O₃ powder (PA 98%), PbO₂ (PA 97%), SrCO₃ (PA 96%), CaCO₃ (PA 99%), CuO (PA 99%), and BaCO₃ (PA 99%). The fabrication of BPSCCO superconductor using solid state reaction method. The synthesis process begins by weighing the materials with a molar ratio of Bi: Pb: Sr: Ca: Cu = 1.6: 0.4: 2.0: 2.0: 3.0. Then mix all the ingredients by crushing using a mortar agate for 3 h. After that the material is calcined at a temperature of 300°C for 6 h. The result of calcination in the form of powder is crushed again for 6 h. Then the calcination was carried out again at a temperature of 820°C for 20 h. The process of calcination up to 2 times aims to release CO₂ gas to produce high-purity oxides. After that each sample was added 1 %wt BaCO₃ and 2 %wt BaCO₃ and crushed for 1 h. The sample was pressed under pressure (p ~ 250 MPa) to form pellets with a diameter of 10 mm and a thickness of 3 mm. The superconducting pellets were sintered in a heating furnace at a constant temperature of 850°C for 30 h with an increase in temperature of 5°C/min. Furthermore, all samples that have become pellets are characterized. Characterization using the Scanning Electron Microscope (SEM JEOL-6390), X-Ray Diffraction (XRD Shimadzu 7000), and Cryogenic Magnet (Instrument Teslatron Oxford).

3. Results and Discussion
3.1. Characterization Using Cryogenic Magnet
Cryogenic magnet tests show the critical temperature (Tc) in the BPSCCO sample with the addition of BaCO₃ (1 %wt and 2 %wt) shown in Figures 1(a) and 1(b). The figures show a relationship between resistance to temperature. It can be seen in the BPSCCO superconductor with the addition of 1% wt BaCO₃, the value of Tc onset is at 86 K and Tc zero is at 52 K, respectively. At the addition of 2% wt BaCO₃ the value of Tc onset is at 80 K and Tc zero is at 23 K. There is a decrease in critical temperature with the increase in the composition of the dopant. The results showed that the BPSCCO superconducting material was dominated by phase 2212 [21]. At Tc onset above 86 K and Tc onset above 80 K, it can be seen that the type of electrical resistance is semiconductor (shown on the downward curve). This shows that the BPSCCO superconducting material is still a semiconductor material [9]. Table 1 shows the addition
of BaCO$_3$ (1% wt and 2% wt) in the superconductor Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_2$O$_{10}$. The highest onset Tc and Tc zero results in the addition of 1% wt BaCO$_3$ dopant to produce T$_{c\text{onset}}$ = 86 K and T$_{c\text{zero}}$ = 52 K. Meanwhile, the addition of 2% wt BaCO$_3$ dopants yields T$_{c\text{onset}}$ = 80 K and T$_{c\text{zero}}$ = 23 K. This proves that the addition of dopants is very influential at critical temperature. The more the BaCO$_3$ composition increases, the more impurity phases are formed, resulting in a decrease in the critical temperature of the sample [12].

### Table 1 Results of Critical Temperature (Tc) Using Cryogenic Magnet.

| Sample Code | Dopant BaCO$_3$ | Sintering | T$_{c\text{onset}}$ (K) | T$_{c\text{zero}}$ (K) |
|-------------|-----------------|-----------|-------------------------|-----------------------|
| Y1          | 1% wt           | 850, 30 h | 86                      | 52                    |
| Y2          | 2% wt           | 850, 30 h | 80                      | 23                    |

![Figure 1](image.png)

**Figure 1.** Relation of Resistance to Temperature Y1 Sample and Y2 Sample.

3.2 Characterization Using SEM-EDX

SEM - EDX test results showed the microstructure of the BaCO$_3$ doped BPSCCO sample (1%wt and 2%wt) with a magnification of 1000x. Figure 2(a) shows the surface morphology of the BPSCCO superconducting material doping 1%wt BaCO$_3$ with sintering treatment at a temperature of 850°C for 30 h looks not homogeneous, there is agglomeration on each side and in the form of long pieces. On the other hand, if we observe a lot of porosity. Figure 2(b) show 2%wt BaCO$_3$ doping is also not yet homogeneous, but the shape of the pieces which partially melts, although not evenly and thoroughly. And at some point, there were still lumps. This is because when barium carbonate is heated, it loses carbon dioxide and forms barium oxide [10]. However, it is not evenly distributed due to the influence of the sintering time which is only 30 h.
3.3 Characterization Using XRD
In XRD testing, the data obtained were analyzed using Match v1.11 software in accordance with the International Center for Diffraction Data (ICDD) database. The results of XRD analysis can be seen in Figure 3. In the diffraction pattern in the figure, it can be seen the phase formation of Bi0.31Ca5.64Sr4.05Cu17O29, (Bi,Pb)-2223, (Bi,Pb)-2212, BiSrCuO, CaPb, and PbO. The highest peak is the phase Bi0.31Ca5.64Sr4.05Cu17O29 at an angle of 2θ = 31.98° with an intensity of 1296.61 cts. BiSrCuO, CaPb, and PbO phases are impurity phases. XRD phase analysis shows that the sample identifies the dominant phase, namely (Bi,Pb)-2212. The optimum phase (Bi,Pb)-2212 at an angle of 2θ = 31° with an intensity of 593.04 cts and a high volume fraction of 64.71%. However, there is still a phase (Bi, Pb) -2223 which is formed although slightly, namely at an angle of 2θ = 23.39° and 2θ = 48.020° with a volume fraction of 35.29%. These results indicate that the addition of 1 % wt BaCO3 sintering treatment for 30 h can increase the phase (Bi, Pb)-2212 and decrease the phase (Bi, Pb)-2223.
To determine whether a crystal of the Bi-2212 or Bi 2223 phase has been formed, XRD measurements are carried out. Based on the results of XRD measurements, the volume fraction of the Bi phase formed is calculated, with equation (1) [3].

\[
\text{Volume Fraction (\%)} = \frac{\text{Bi Phase Intensity}}{\text{Total Phase Intensity}} \times 100\% 
\]

The following is a comparison of the volume fraction and angle at the highest peak in sample Y1, as can be seen in Table 2.

**Table 2** The Volume Fraction and Phase Angle Formation 2θ in Y1 Sample.

| Phase     | Volume Fraction (%) | 2θ (Degree)/Intensity (cts) |
|-----------|---------------------|-----------------------------|
| Bi - 2212 | 64.71               | 31                          |
|           |                     | 593.04                      |
| Bi - 2223 | 35.29               | 23.39                       |
|           |                     | 148.16                      |

**Conclusion**

Based on the results obtained from this study, it can be concluded that the effect of adding BaCO\(_3\) to the Bi-Pb-Sr-Ca-Cu-O superconductor affects the critical temperature (T\(_c\)) formed. The addition of 1%wt BaCO\(_3\) results in a higher critical temperature than adding 2%wt BaCO\(_3\). There was a decrease in critical temperature (T\(_c\)) as BaCO\(_3\) increased. The optimal critical temperature (T\(_c\)) produced, T\(_c\)\(_\text{onset}\) = 86 K and T\(_c\)\(_\text{zero}\) = 52 K. The sample shows the presence of semiconductor properties at temperatures of 86 K and above. However below 86 K these samples exhibit superconducting properties and reached zero electrical type resistance at temperatures below 52 K. In this sample, the dominant phase formed is phase (Bi-Pb) -2212, but there is also a phase (Bi, Pb) -2223 with a small amount on volume fraction.

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