The Effect of Sintering Time on The Formation of The BPSCCO-2212 Superconductor Phase at The Levels of Ca=1.10 Using The Wet Mixing Method

Retno Asih(a), Suprihatin(b), and Simon Sembiring

Department of Physics, University of Lampung, Bandar Lampung, Indonesia, 35141

Abstract

This research was conducted to determine the effect of sintering time on to phase formation of superconducting BPSCCO-2212 with Ca content 1.10 by calculating the level of purity of the phases formed and looking at the microstructure. The variation of sintering time was 10, 20, 30, and 40 hours using the wet mixing method. The sample was calcinated at 800 °C for 10 hours and sintered at 830 °C. The XRD’s characterization result showed that the highest volume fraction obtained in BPSCCO-2212/40 hours was 86.72%, while the lowest volume fraction of BPSCCO-2212/30 hours was 53.07%. The relatively high orientation degree of BPSCCO-2212/30 hours was 13.59%, while the lowest orientation degree of BPSCCO-2212/20 hours was 7.67%. The SEM’s characterization result shows that all samples have not been oriented, and many voids (space between the plates) are still generated.

1. Introduction

Superconductors are materials that can conduct electric current without any resistance or resistance ($\rho = 0$) so that they can conduct electric current without the slightest loss of power. Since the discovery of superconducting materials by Dutch physicists from Leiden University HK Onnes in 1911, research on superconducting materials has continued to develop. Superconductors are increasingly being used along with technological advances, such as the super-fast trains in Japan known as MagLev (Magnetic Levitation) trains (Shimbashi and Minato-ku, 2003).

Research on superconductors is intensively carried out to comprehensively understand physical problems related to theoretical, experimental, and application aspects. One of the widely studied SKST materials is the Bi-Sr-Ca-Cu-O (BSCCO) system because its critical temperature is relatively high and does not contain toxic elements.
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(Yulianti, 2002), they are also known as Bi-based superconductors. There are 3 phases in this system. The different superconductive ones are phase 2201 with $T_c = 10$ K, phase 2212 with $T_c = 80$ K, and phase 2223 with $T_c = 110$ K.

Synthesis of superconducting crystal Bi-2212 can be achieved through several methods, including the solid phase reaction method, the Floating Zone (FZ) method, the Self Flux method with Pb doping (Zhao et al., 2000), the SelF Flux method with CaCO$_3$ and CuO (Yulianti, 2002), and the Traveling Solvent Floating Zone (TSFZ) method (Benseman et al., 2007). Generally, these methods produce powders with a crystal size of >100 nm and require a relatively long heating time.

Dopants play an essential role in the formation of high Tc superconductors. Increasing the value of critical temperature and critical current density can be done by giving a dopant (DB Currie and AM Forest, 1988). The dopant can replace the original atoms in the superconductor with dopant atoms that are not much different in size from the original atoms. In addition, the dopant can be added. That is, adding dopant atoms to the original atoms of the superconductor. The use of Pb dopants in the synthesis of polycrystalline Bi systems, apart from facilitating the formation of the compound in question, also affects the properties of the resulting compound. Due to the similarity of ion sizes and valence requirements of Pb atoms, it is believed that the addition of Pb as a dopant results in the substitution of Bi atoms by Pb atoms in the Bi-O double layer (Nurmalita, 2011).

Research on Pb doping variations in the BPSCCO 2212 system was conducted by Pratiwi (2016) with variations in Pb doping levels used 0; 0.1; 0.2; 0.3, and 0.4, at Ca content 1.10, calcination temperature 800°C and sintering temperature 830°C, using the solid reaction method. This study found that samples with a doping level of 0.4 had the highest volume fraction ($F_{v} = 89.99\%$) and degree of orientation ($P = 23.16\%$).

Then research on the effect of sintering temperature on CaCO$_3$ levels 1.10 was carried out by Sari (2013) by varying the sintering temperatures to 815°C, 820°C, 825°C, 830°C using the solid reaction method. The results showed that the highest volume fraction was obtained at 830°C sintering temperature, namely $F_{v} = 90.10\%$, while the highest degree of orientation was obtained at 825°C, namely $P = 59.31\%$.

This study aims to determine the effect of sintering time on the purity level of the BPSCCO-2212 superconducting phase at Ca content of 1.10 using the wet mixing method with variations of sintering time 10 hours, 20 hours, 30 hours, and 40 hours. The aspect studied in this research is the purity level of the formed phase by calculating the volume fraction value, orientation degree, and impurities. The results obtained were characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2. Research Methods

In this study, oxides and carbonates were used with a high level of purity, namely: Bi$_2$O$_3$ (99.9%); PbO (99.9%); SrCO$_3$ (99.9%); CaCO$_3$ (99.9%); CuO (99.99%), HNO$_3$, equates, and HCl. The composition of the starting materials for making 3 grams of superconducting sample BPSCCO-2212 is presented in Table 1. The tools used in this study were: digital sartorius balance, grinding tool (paste and mortar), furnace, the crucible, spatula, sample mold (die), pressing tool, X-Ray Diffraction (XRD) type X'Pert Powder Diffractometer, and Scanning Electron Microscopy (SEM) Type Vega Tescan.

The basic materials used in this study were weighed first according to the calculations in Table 1. After the material was weighed, then the material was dissolved with 68% nitric acid (HNO3), and distilled water was stirred slowly until the solution was clear blue. The material was placed on a hot plate at 70 °C. Then, the solution was allowed to stand for 24 hours until the solution stirred. Drying was carried out gradually in a furnace at temperatures 300, 400, and 600 °C until the material was dehydrated.

After the material was dried in the furnace, grinding was carried out with mortar and pestle gradually for ±10 hours until the material feels smooth. The sample was compacted with a pressing tool with a strength of 8 tons. After the sample is in the form of pellets, it is then calcined at a temperature of 800 °C for ±10 hours. The calcined sample was not perfect due to the porosity and surrounding gas capture, so it needed to be re-ground for ±10 hours. Then the sample was re-compacted and sintered with time variations of 10, 20, 30, and 40 hours at a temperature of 830°C to form the desired phase.

The results of the superconductor synthesis were then characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD characterization aims to determine the level of phase purity by calculating $F_{v}$, $P$, and I using the equation (1) to (3).

Table 1. Material composition Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_{1.1}$Cu$_3$O

| Starting Material | Fraction | Mass Count Each 3 gr sample (gr) |
|-------------------|----------|----------------------------------|
| Bi$_2$O$_3$       | 1.6      | 1.2353                           |
| PbO               | 0.4      | 0.1315                           |
| SrCO$_3$          | 2.0      | 0.8687                           |
| CaCO$_3$          | 1.1      | 0.2948                           |
| CuO               | 2.0      | 0.4686                           |
| Total             |          | 3,0000                           |

\[
F_{v} = \frac{\sum(A_{2212})}{\sum(A_{total})} \times 100\% \quad (1)
\]

\[
P = \frac{\sum(A_{Ca})}{\sum(A_{total})} \times 100\% \quad (2)
\]

\[
I = 100\% - F_{v} \quad (3)
\]
where

\[ F_v = \text{BPSCCO-2212 phase volume fraction} \]

\[ P = \text{degree of orientation} \]

\[ I = \text{Impurity} \]

\[ I_{\text{total}} = \text{Total intensity} \]

\[ I_{\text{2212}} = \text{Phase intensity 2212} \]

\[ I_{\langle 001 \rangle} = \text{BPSCCO-2212 phase intensity, with } h = k = 0 \text{ and } l \text{ an even number} \]

XRD spectrum analysis was performed using the High Scoreplus program. SEM characterization aims to determine the microstructure of the BPSCCO-2212 superconductor.

3. Results and Discussions

3.1 Results of Characterization of X-Ray Diffraction (XRD)

To facilitate data presentation and analysis, each sample was coded based on the sintering time indicating the parameters of the synthesis process in the following format: BPSCCO-2212/10 hours indicates that the BPSCCO-2212 superconducting sample sintered for 10 hours.

The results of the XRD spectrum analysis of the BPSCCO-2212 sample are shown in Figure 1. Based on Figure 1, all the samples that have been synthesized succeeded in forming the BPSCCO-2212 phase, although they still did not form a pure BPSCCO-2212 phase, or many impurities appeared. In addition, all samples were oriented, indicating the presence of BPSCCO-2212 phase peaks with \( h = k = 0 \) and \( l \) = even numbers. The results of the analysis of the High Scoreplus program and calculations using equations 1, 2, and 3 obtained the level of phase purity which includes volume fraction \( (F_v) \), degree of orientation \( (P) \), and impurity \( (I) \) for each sample.

Based on Figure 1, the resulting peaks consist of BPSCCO-2212 superconducting peaks and impurities. The BPSCCO-2212 peak is symbolized by A, while the impurity is symbolized by B and C. In general, all of the synthesized samples succeeded in forming the BPSCCO-2212 phase, although they still did not form a pure BPSCCO-2212 phase or many impurities appeared.

The BPSCCO-2212/10-hour sample formed 14 highest peaks with eight prominent peaks of BPSCCO-2212; four were impurities, \( \text{Ca}_{0.95}\text{Sr}_{2}\text{Bi}_{0.95}\text{O}_{4}\text{Ba}_{0.12}\text{Cu}_{0.88} \text{O}_{4} \), and two peaks were impurities \( \text{Bi}_4\text{O}_9 \). In the BPSCCO-2212/20 hour sample, 18 highest peaks were formed with nine prominent peaks of BPSCCO-2212, four were \( \text{Bi}_{2223} \) impurities, and 5 were compounds \( \text{Ca}_{0.95}\text{Sr}_{2}\text{Bi}_{0.95}\text{O}_{4}\text{Ba}_{0.12}\text{Cu}_{0.88} \text{O}_{4} \). Then, the BPSCCO-2212/30-hour sample formed 17 highest peaks with ten prominent peaks of BPSCCO-2212, two peaks were \( \text{Bi}_{2223} \) impurities, three were \( \text{Ca} \) compounds \( \text{Cu}_{0.95}\text{Sr}_{2}\text{Bi}_{0.95}\text{O}_{4}\text{Ba}_{0.12}\text{Cu}_{0.88} \text{O}_{4} \), and two peaks were impurities \( \text{Bi}_4\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Cu}_{0.88} \text{O}_{4} \). In comparison, the BPSCCO-2212 / 40-hour sample formed 18 highest peaks with 14 prominent peaks of BPSCCO-2212 and four impurity peaks \( \text{Bi}_4(\text{Sr}_2\text{Ca}_{0.6})\text{Cu}_{0.88} \text{O}_{4} \).

The addition of sintering time to the sample can affect the phase formation in the BSCCO system (Nurmalita, 2011). Based on the results of XRD analysis, the purity of the BPSCCO-2212 phase formed in the form of volume fraction \( (F_v) \), orientation degree \( (P) \), and impurity \( (I) \), as shown in Table 2 and Table 3 shows that the sintering time is exceptionally influential on the formation of the superconducting phase of BPSCCO-2212. It can be seen in Table 2 that the value of the volume fraction is opposite to the value of the impurity. In BPSCCO-2212, with a sintering time of 40 hours, the highest volume fraction value was 86.72\%, and the lowest impurity was 13.28\%. Meanwhile, in BPSCCO-2212, with a sintering time of 30 hours, the lowest volume fraction value was 53.07\%, and the highest impurity was 46.93\%. In addition, BPSCCO-2212, with a sintering time of 10 hours, obtained a volume fraction value of 66.21\%, and BPSCCO-2212, with a sintering time of 20 hours, had a volume fraction value of 59.66\%. However, it is only sometimes possible to increase the sintering time to increase the volume fraction. Excess can form an impurity phase. This effect affects the formation of a phase with a sintering time of 30 hours BPSCCO-2212.

This research using the wet mixing method produces peaks that are clearer than the solids method carried out by Pratiwi (2017). The volume fraction results obtained in this study were 67.80\% at a sintering time of 20 hours. Meanwhile, in this study, the volume fraction obtained at 20 hours of sintering was 59.66\% and the highest volume fraction obtained at 40 hours of sintering was 86.72\%. This shows that the synthesis of superconductors using the wet mixing method can increase the high homogeneity to get a higher phase purity.
Table 2. Results of calculation of volume fraction and impurities

| Sample Code | Phase Intensity 2212 | Total intensity | Volume fraction (%) | Impurities (%) |
|-------------|-----------------------|-----------------|---------------------|----------------|
| BPSCCO-2212/10 hours | 4959.4596 | 7490.5841 | 66.21 | 33.79 |
| BPSCCO-2212/20 hours | 3806.9762 | 6381.5696 | 59.66 | 40.34 |
| BPSCCO-2212/30 hours | 24430.2609 | 32082.2882 | 53.07 | 46.93 |
| BPSCCO-2212/40 hours | 19714.733 | 24934.558 | 86.72 | 13.28 |

Table 3. Orientation degree calculation result

| Sample Code | $\theta$ | hkl (00 l) | Intensity (00 l) | Degree of Orientation (%) |
|-------------|----------|------------|------------------|---------------------------|
| BPSCCO-2212/10 hours | 60.9618 | 00 20 | 427.5377 | 8.62 |
| BPSCCO-2212/20 hours | 53.9902 | 00 16 | 292.1312 | 7.67 |
| BPSCCO-2212/30 hours | 23.3332 | 00 8 | 430.4325 | 13.59 |
| BPSCCO-2212/40 hours | 23.1423 | 00 8 | 943.1525 | 11.67 |

3.2 Scanning Electron Microscopy (SEM) Characterization Results

Microstructure testing was carried out on all BPSCCO-2212 superconducting samples at various sintering times using Scanning Electron Microscopy (SEM). Each sample was recorded at a magnification of 2000×. The results of the SEM recording are shown in Figure 2.
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**Figure 2.** Results of Scanning Electron Microscopy (SEM) characterization (a) BPSCCO-2212/10 hours; (b) BPSCCO-2212/20 hours; (c) BPSCCO-2212/30 hours; (d) BPSCCO-2212/40 hours.

Based on Figure 2, all samples did not show oriented layers. In addition, the samples showed poor crystal formation, and there were still lots of empty spaces between the plates (voids). The plates were seen to be oriented shown in Figure 12 (c), namely the BPSCCO-2212/30-hour sample. This follows the resulting orientation degree value of 13.59%. Meanwhile, the results that could be better oriented are shown in Figure 12 (b). It can be seen that many of the characterization results have yet to form unidirectional plates with a degree of orientation value of 7.67%. The degree of orientation resulting from variations in the sintering time is irregular. It follows the SEM characterization results, which show that the plate image is also not improving.

4. **Conclusion**

Based on the results of XRD characterization, the highest volume fraction was obtained at a sintering time of 40 hours BPSCCO/40 hours at 86.72%. Meanwhile, at a sintering time of 30 hours BPSCCO/30 hours, the lowest volume fraction value was 53.07%.

In addition to the BPSCCO-2212 phase, other phases were obtained, namely BPSCCO-2223 and other impurities, at sintering times of 10, 20, 30, and 40 hours.

The SEM test results show that the variation of sintering time affects the surface morphology of the resulting more homogeneous superconductor and the plates tend to be oriented (oriented) based on the results of the degree of orientation produced with the highest value of BPSCCO-2212/30 of 13.59% and the lowest degree of orientation of BPSCCO-2212/ 20 hours by 7.67%.

5. **Bibliography**

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