Study on Cold-Drawing in Powder-in-Tube Process in Fabricating Silver-Sheathed (Bi,Pb)-Sr-Ca-Cu-O Tapes

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Abstract. Since Cu oxide superconductors have been discovered, the application for this type of superconductor especially in the form of superconducting tape to be used as electric cable to transport the electricity. The aim to this study is to analyse the manufacture of superconducting wire with superconducting pellets as its precursor. A pellet disc of High Temperature Superconducting (HTS) Bi,Pb-Sr-Ca-Cu-O has been made by using solid state method. This pellet has been prepared by mixing each of oxide powders together, and then sintered at 865°C for 90 hours. We have analysed the samples using X-Ray Diffractometer (XRD), Energy Dispersive x-ray Spectroscopy (EDS), Scanning Electron Microscopy (SEM) and also resistivity measurement to confirm its superconductivity. After confirmed the superconducting properties of the pellet, it was grinded into powder and inserted into silver tube with outer diameter of 10 mm and thickness of 1 mm. And then, drawn to make monofilament wire. It were then cut and inserted into another silver tube, and then re-drawing and rolled into multifilament tapes using Powder-in-Tube (PIT) method. The multifilament tapes was heated at 850°C for 12 hours. We confirmed its phase crystalline and superconductivity at pellet disc. However, when the pellet disc was made into wire and sintered at 850°C, it became amorphous and conductivity behaviour was decline. According to SEM analysis and resistivity measurement result, silver also penetrated inside the sample region of multifilament wire.

1. Introduction
Superconductors have big potential to be applied in practical equipment when it is in the form of wire. Since Cu-O type superconductor was discovered on 1986, Bednorz and Muller [1], research on superconducting wires has attracted much attentions among scientists. These type of superconductors have critical temperature above nitrogen liquid (77K). So, it will increase their possibility to be used in practical application. Also, the great demand for application of superconductivity promotes the need for wire superconductor [2].

In this research, the superconductor used is of Bi,Pb-Sr-Ca-Cu-O (or so-called BPSCCO). In making superconducting wire, solid state reaction is used and raw materials are powders form which a pellet disc of superconducting BSCCO can be fabricated [3]. The crystal structure was investigated when superconducting filaments had been made from its pellet by PIT method.
Figure 1 shows the crystal structure of three phases of Bi-Sr-Ca-Cu-O (BSCCO). Phase 2201 has space group of Ama2 with a = 5.36200 Å, b = 5.37400 Å, and c = 24.6220 Å. Phase 2212 has space group of I4/mmm with a = b = 3.82500 Å, c = 30.8200 Å. Phase 2223 has space group of I4/mmm with a = b = 3.82300 Å, c = 37.3740 Å. Pb substituted Bi on the phase 2223. These were illustrated using crystal drawing application of VESTA. Pb atoms substitute Bi atoms on the phases of 2223 and 2212. Each element has its layer of oxide. These phases were determined by the sum of Cu-O layers of its unit cell [4].

The 2201, 2212 and 2223 phases have transition temperature of 20 K, 95 K and 110 K, respectively. This research aims to study the effect of cold drawing using ground pellet superconductor as precursor in order to make superconducting wire. Superconducting wire is predicted to be used in power devices such as motor, transformer, generator and electric cable. In case of BSCCO superconductor, the application is especially for power electric cable [3].

2. Method of Sample Preparation
A disc pellet of superconducting BSCCO was carried out by solid state reaction. Fabrication in the form of wires required superconductors in powders form as precursor materials. Therefore, superconducting powders was made by grinding pellet of superconductor. The phase 2223 has narrow forming temperature range (840°C to 880°C); therefore, adjustment of temperature in the furnace is critical [5,6].

BPSCCO pellet superconductor was made through solid state reaction. Raw material used were powders of: Bi2O3, PbO, SrCO3, CaCO3, and CuO. Drying was followed by heating 200°C for 2 hours for each element to remove its vapors.

Before calcination, drying was done in temperature of 300°C for 10 minutes. Weighing followed by compaction with a press machine was conducted. Based on stoichiometry results, in order to get the phase of Bi1.6Pb0.4Sr2Ca2Cu3O8+α, the weight ratio of materials should be: Bi2O3 : PbO : SrCO3 : CaCO3 : CuO = 9.34 : 2.24 : 7.41 : 5.02 : 5.98.

These powders were mixed together for 5 hours [7,8]. Mixed powder was pressed and heated at 820°C for 19 hours. After it has been cooled into room temperature, it was ground into powder, pressed and then sintered. The increase in temperature, the holding time, and the decrease in temperature of sintering can be seen in Figure 2. From room temperature, heating was carried out up to temperature of 865°C reached about 3 hours [6]. After that, temperature was held for about 90 hours. Cooling to room temperature in the furnace was reached in about 24 hours.
Figure 2. Heating and cooling rates as well as holding time during sintering process

Final pellet sample has diameter of 10 mm and thickness of about 2 mm. Morphological analysis of the sample was performed using Scanning Electron Microscopy (SEM). The equipment allows semi-quantitative analysis of the samples by X-ray microanalysis with an Energy Dispersive detector (EDS). Sample was also analyzed by X-ray diffraction. Resistivity measurement was conducted using four-point probe method of cryogenic magnet system (Oxford Cryotron).

After synthesizing and confirming the superconducting properties of the pellets, a wire was manufactured through Powder-In-Tube (PIT) method.

Figure 3 illustrates the process flow of making superconducting wire

Figure 3. Process flow of making superconducting wire

After the confirmation of superconducting properties, the pellet was ground into powder and inserted into silver tube, drawn and packed into bigger silver tube. The last silver tube was then re-drawn and rolled into wire [9].

The elemental composition, crystal structure, morphology, and electrical properties of the multifilament wire were also investigated with EDS, SEM, XRD and resistivity measurement methods.
Figure 4. Cross section of Multi filament (a) before been drawn and rolled (photograph), and (b) after been drawn, rolled and sintered (SEM analysis)

Figure 4 shows the cross section of multi filament before and after the drawing, rolling and sintering. Figure 4 (a) shows 27 monofilaments after insertion into the silver tube. This multifilament billet was drawn and rolled into multifilament wire. Figure 4 (b) shows cross sectional of multifilament wire analyzed with SEM.

3. Result and Discussion
A disc pellet of superconducting BSCCO was carried out by solid state reaction. Fabrication in the

3.1. XRD Analysis

Figure 5 shows the XRD analysis of pellet, powder (ground pellet), monofilament (after drawing/rolling and before sintering) and multifilament (after sintering at 850°C for 12 hours).

It was observed that formation of main structure of phase 2212 was detected. This formation was also accompanied by minor structure of Sr2Bi2O5. XRD analysis also shows the phase of 2223 within the sample [10].

These XRD peaks were investigated with Rietveld method to analyze the percentage of its phases in the pellet. The results show that 2223 phase has the portion of 47% and 2212 phase has 36.4%. While in the multifilament, 2223 and 2212 phases both have the portion of 0%. It means that 2223 and 2212 phases in the multifilament have become amorphous. Only the peaks of silver, i.e. silver tubes, were found in the multifilament sample. The peaks of silver are accentuated, as the silver tubes experience elongated deformation during wire-drawing and their corresponding crystallographic textures become more oriented.
3.2. SEM/EDS Analysis

Figure 6 points out the analysis result of SEM on the sample surface. This SEM analysis observes the non-uniform phase on its surface. But some areas show layer structure estimated belonging to crystal structure of BPSCCO system. Sample also forms a porous material.

![Figure 6](image.png)

**Figure 6.** SEM analysis of pellet of (a) 500 times,(b) 2000 times and (c) 4000 times of enlargement. Sample forms porous material.

![Figure 7](image.png)

**Figure 7.** Counted particle size of the pellet (a) the thick of particles (c-axis of crystal) and (b) the width of particles (ab plane of crystal)

Figure 7 shows the counted particle size of the sample. Figure 7(a) shows the thickness of particle, whereas figure 7(b) shows the length of particle. The sample forms layers of particles. According to its crystal structure, the width of layer is correlated with the ab plane, while the thickness of layer is correlated with the c axis of its crystal structure [11].

The particle length in the ab plane (i.e. the particle width) is around 6.46 µm ± 2.43 µm whereas the particle length in the c-axis (i.e. the particle thickness) is around 0.67µm ± 0.23 µm.
Figure 8. Distribution of elements of Bi, PbSr, Ca, Cu, O and Ag in multifilament sample.

Figure 8 shows the mapping of Bi, Pb, Sr, Ca, Cu, O and Ag in the multifilament sample. According to this analysis, it is noted that Bi, Pb, Sr, Ca, Cu has similar pattern of uneven distribution. This shows that although sample has formed crystals in the pellet form, the dissociation of compounds in the multifilament sample occurs.

Figure 9 shows the SEM analysis of multifilament sample.

Figure 9 shows the SEM analysis of multifilament sample. The crystal like particles that has been observed in pellet sample were not observed in multifilament one. By comparison with figure 8, it is also shown that the silver has infiltrated into the region of BPSCCO.

The BPSCCO crystal was formed in pellet, but such crystal became amorphous after sintered at 850°C for 12 hours. Silver also could be found inside the sample. Silver is supposed to melt and diffuse inside sample since its melting temperature (Tm = 961°C) is close to the sintering temperature.
Table 1. Elements composition (EDS analysis)

| Element | Pellet Mass % | Atom % | Multfilament Mass % | Atom % |
|---------|--------------|--------|--------------------|--------|
| O       | 7.84         | 30.20  | 10.89              | 36.93  |
| Ca      | 7.06         | 10.85  | 10.26              | 13.89  |
| Cu      | 39.54        | 38.34  | 40.25              | 34.38  |
| Sr      | 17.54        | 12.34  | 9.35               | 5.78   |
| Ag      | 6.50         | 1.94   | 5.87               | 1.53   |
| Bi      | 21.52        | 6.34   | 17.48              | 4.53   |

Table 1 shows the elemental composition of Bi, Pb, Sr, Ca, Cu, O and Ag in pellet and multifilament samples. There is no big difference between pellet and multifilament. In general Ca content in both pellet and multifilament forms is higher than that of Pb, whereas the Cu content is higher than those of Bi and Sr. In multifilament sample, Ag also was found in the region of BPSCCO.

3.3. Resistivity Analysis

Resistivity was measured using the four-point probe method. In order to expose it to the electrical current, the sample was connected to the cryogenic system through four terminals and glued using Ag paste. Cryogenic cooling system was utilized to reach low temperature environment.

Figure 10 shows the temperature dependence of resistivity of pellet sample. The resistivity starts to drop around 108 K. And it reached zero around 98 K. Hence the sample has been confirmed to have a superconductivity behavior. Figure 10(b) shows the gradient of resistivity vs temperature around the critical temperature. There is a clear peak at the temperature of 105 K.

The resistivity of conducting material can be analyzed by Matthiessen’s rule [12,13,14]:

\[ \rho(T, c) = \rho_0(c) + \rho_i(T) \]  

(1)

Where \( \rho_0(c) \) is the residual resistivity due to defect scattering and is essentially temperature independent, and \( \rho_i(T) \) is the temperature-dependent part of the resistivity (or intrinsic resistivity).

The temperature-dependent part of the resistivity can be analyzed using Bloch-Grüneisen formula [15,16].

\[ \rho_i(T) = \frac{c}{m \cdot \theta} \cdot \left( \frac{T}{\theta} \right)^5 \int_{0}^{\theta} \frac{z e^z}{(e^z - 1)^2} dz \]  

(2)
Where $T$ is temperature, $\theta$ is characteristic temperature of metal known as the electric resistivity Debye temperature, $M$ is the atomic weight, and $C$ is a constant of the metal. For silver resistivity, Matthiessen’s rule becomes [12,17]:

$$\rho(\sigma,T) = 3.3 \times 10^{-7} (\text{Ohm. cm}) + \rho_1(T)$$  \hspace{1cm} (3)

If, $x = \frac{\theta}{T}$, the intrinsic resistivity can be expressed as Grüneisen function, $F(x)$. [18]

$$F(x) = \frac{4}{x^3} \int_0^x \frac{z^2e^x}{(e^z-1)^2} \, dz$$  \hspace{1cm} (4)

Figure 11 shows the temperature dependence of resistivity of monofilament sample. There is no resistivity drop observed. It shows only conductor behavior along with temperature. Figure 11b shows the resistivity analysis along with the plot of Grüneisen function for silver. Sample has larger resistivity compared to Grüneisen function. This result indicates that the silver has been contaminated and has high residual resistivity.

Figure 12 shows the temperature dependence of resistivity of multifilament sample. There is no resistivity drop observed. Figure 12b shows the resistivity analysis along with the plot of Grüneisen function for silver. Sample has larger resistivity compared to Grüneisen function. This result indicates that the silver has been contaminated and has high residual resistivity. The residual resistivity in this sample is much higher than that in the monofilament one.
To analyze the conductivity behavior of both samples, the residual resistivity ratio (RRR) was calculated using the following equation,

\[ RRR = \frac{\rho(293K)}{\rho(4.2K)} \ldots \] (5)

RRR for monofilament sample is 6.21, and for multifilament sample is 0.87. It indicates that the multifilament sample has higher impurity than monofilament sample does. This suggests that in the process of making multifilament, the conductivity properties of silver was decreased, which is expected to occur due to high sintering temperature.

4. Conclusion

The pellet sample of BPSCCO was made by a solid state reaction, and used as precursor to make wire superconductor. The superconductor pellet was sintered at 865°C for 90 hours. The sample has phases of 2223 and 2212, with the critical temperature of 110 K. However, when it was used as precursor for making superconducting wire, the material lost its superconductivity. This situation is believed to occur due to the change of its crystallinity into amorphous state, when the sample was ground and sintered. Silver also was found to infiltrate material. Based on the results of resistivity measurements on monofilament and multifilament samples, it appears that the resistivity value of the samples are above the plot of Grüneisen function of the silver, which indicates that the samples have high residual resistivity. This result also indicates that the silver has been contaminated.

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