Superconducting properties of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (BSCCO-2223) superconductor ceramics prepared by conventional solid-state reaction and co-precipitation methods

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Abstract. The (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (BSCCO-2223) samples were prepared by conventional solid-state reaction and co-precipitation methods. The crystal size, cell parameter, and crystal structure were identified from X-ray diffraction (XRD). The peaks drawn by co-precipitation have higher intensities and the width of peaks were narrower compared to the sample prepared by solid-state method. Slight difference in the value of lattice parameters between the samples were also noticeable. Concentration of defects increased the distortion of crystal lattice that cause the changes in these parameters. The electrical properties of the superconductors were investigated by using cryogenic four-point probe and AC susceptibility. The sample prepared by co-precipitation method was able to reach higher critical temperature, $T_C$ at 106 K compared to the other sample, $T_C$ at 97 K. Meanwhile Scanning Electron Microscope (SEM) micrographs for solid-state method sample showed more random grain alignment and porous structures. The microstructures and grain growth results of Bi-2223 were reflected to the heat and temperature applied during sintering process. In short, the research work reveals that co-precipitation method produces better quality of high temperature superconductor compared with solid-state method due to higher homogeneity resulted by chemical reactions.

1. Introduction

The discovery of superconductivity of BSCCO family has attracted interest of researchers from all over the world. These materials have special ability which is to carry current with zero resistance and reduce power loss during the process of transmitting electricity [1]. In electrical transmission system, superconducting wire is used to produce a transmission cable. It is proven that the distinctive properties of superconductor enable the development of high efficiency energy devices. Several others electrical power devices such as motor, generator, fault current limiter and magnetic storage system have been developed [2-4].

In order to produce high quality material in large-scale manufacturing, it will depend mainly on the process conditions for the production of the BSCCO powders. The most practical technique for the production of BSCCO powders is the solid-state reaction method. The main issue of using this method is the repetition of grinding process for several times before the sintering process. It is necessary to achieve end products with fine particle size, homogeneity, high purity and with the desired superconducting properties [5]. Then, heat treatment plays an important role in the fabrication of pure...
Bi-2223 bulk samples since it will diminish several unwanted phases such as Bi-2212, Bi-2201 and Ca$_2$PbO$_4$ [6–8].

The co-precipitation method is another approach of producing BSCCO oxide powder which requires precise control of the reaction environment (pH). The powders obtained by the co-precipitation techniques have a smaller grain size and has higher homogeneity than the powders of the solid-state reaction method. Existence of impurities will directly reduce the value of $T_C$ and $J_C$ of the samples since these impurities are located within the grains and limit the grain connectivity [9].

The bulk samples of Bi-2223 were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for their phase purity, homogeneity, grain size and orientation, while the superconducting properties were tested by ac susceptibility and four-point dc-electrical resistivity methods. Throughout this investigation, a comparison of the co-precipitation and the solid-state reaction methods regarding their process conditions and the quality of the powders produced was achieved.

2. Experimental

First specimen with nominal composition Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ was prepared via conventional solid-state method. Samples were made of oxide and carbonate powders, homogenously mixed according to its stoichiometric molar ratio of Bi$_2$O$_3$, PbO, Sr$_2$CO$_3$, CaCO$_3$ and CuO. The mixture was ground and heated twice in a tube furnace with free air flow at temperature of 810°C for 30 hours to remove impurities and form the Bi-2223 oxide. According to V.Garnier, the calcined powder phase assemblage is sensitive to the calcination conditions, and control of the calcination parameters is necessary to form the adequate reactive secondary phases (Bi-2212, Ca$_2$PbO$_4$, Ca$_2$CuO$_3$, CuO). These phases are necessary for the proper synthesis of Bi-2223 during the sintering step [10]. Then, the oxide powder was pressed at room temperature with pressure of 7 tonnes. Bulk sample of 13 mm in diameter and 3 mm in thickness was formed and synthesized under the same condition at 850°C for 60 hours, then furnace-cooled to room temperature.

The second specimen was produced by co-precipitation method described by Hamadneh et al. [11]. All the chemical powders were acquired from Sigma-Aldrich, USA. Then, the precursor’s oxide powder was pelletized and sintered to achieve the required Bi-2223 phase. The dehydrated powder was thoroughly mixed and grounded in an agate mortar. After the first grounding process, the compound went through pre-calcine process at temperature of 730°C for 12 hours. Then, after the second grounding process, the powder was calcined at temperature of 850°C for 24 hours. Next, the powder was then pressed into pellet under hydrostatic pressure around 7 tons or 70,000 psi. The pellets were sintered at maximum heat of 850°C for 48 hours and then furnace-cooled to room temperature.

Phase identification of both specimens were conducted using a Bruker D8 Advanced X-Ray Diffractometer (XRD). Microstructure investigation was carried out using a Hitachi S3400N Scanning Electron Microscope (SEM). Superconducting properties for each sample, such as transition temperature, $T_C$ and the critical current density, $J_C$ were determined by using AC susceptibility technique.

3. Results and Analysis

Figure 1 and Figure 2 show XRD spectrums for Bi-2223 bulk sample prepared by solid-state and co-precipitation methods. Multiphase structure was observed in both samples which indicates the difficulty in obtaining a single-phase material. This can be attributed to the phase transition between Bi-2201, Bi-2212 phase, and also the orientation of the grains. The number of corresponding peaks and their intensities indicates that the high $T_C$ phase is the dominant phase in both samples.
Figure 1. XRD for Bi-2223 bulk sample prepared by solid-state method.

Figure 2. XRD for Bi-2223 bulk sample prepared by co-precipitation method.
Table 1 shows value of lattice parameters for both samples. The values are in agreement with the previous investigators where the parameters value obtained were still within the range [12-13]. In view of results from XRD and lattice parameters, those intense peak patterns of sample belong to the high-T\textsubscript{c} phase, which also indicates an increase in the volume fraction of the Bi-2223 phase. Volume fraction of Bi-2223 for sample prepared by solid-state method can be increased by extending the period of sintering time.

**Table 1.** Lattice parameter for samples prepared by solid-state and co-precipitation methods.

| Lattice Parameter | Solid-state Method | Co-precipitation Method |
|-------------------|--------------------|------------------------|
| a                 | 5.266 Å            | 5.408 Å                |
| b                 | 5.471 Å            | 5.408 Å                |
| c                 | 38.301 Å           | 37.015 Å               |

Sintering time and temperature influence Bi-2223 volume fraction. These parameters also play significant role in improving the grain coupling, the grain morphology, and the phase formation and transition, leading to the improvement of the electrical properties of Bi-2223 [14-15]. Figure 3 and Figure 4 show T\textsubscript{c} measurement using four-point probe for the samples. Critical temperature for sample prepared by co-precipitation method was recorded at 102 K, compared to sample prepared by solid-state method which was at 95 K. Sample with higher T\textsubscript{c} value usually has stronger link between the grains, which can be spotted later in SEM analysis by observing the grain’s alignment along the c-axis. It is known that the composition variation at the grain boundaries, disoriented grain is one of the mechanisms that control the weak link behavior of polycrystalline high-T\textsubscript{c} superconductors [16]. S.M. Cassidy also reported that the temperature and field dependence of the grain boundary weak link dissipation in BSCCO tapes drops rapidly as the temperature decreases [17].

![Graph showing electrical resistance vs. temperature](image-url)
Figure 4. $T_C$ measurement using four-point probe for Bi-2223 bulk sample prepared by co-precipitation method.

AC susceptibility has been used to measure the critical temperature and critical current of the samples. Figure 5 and Figure 6 show the real parts of susceptibility ($\chi'$) of both samples, solid-state method and co-precipitation method, respectively. In each graph, the position of inflection point on the curve is the critical temperature. This is due to the considerable difference between lower critical magnetic field of the intergranular matrix and the grains, because the flux will penetrate the intergranular matrix first before it reaches the grains [18].

Figure 5. Real ($\chi'$) parts of susceptibility for Bi-2223 bulk sample prepared by solid-state method, applied magnetic field, $H_a=50$e and frequency of 295Hz.
Figure 6. Real ($\chi'$) parts of susceptibility for Bi-2223 bulk sample prepared by co-precipitation method, applied magnetic field, $H_a=5$ oe and frequency of 295Hz.

At temperature of 77 K, critical current density, $J_C$ for solid-state sample was recorded as 1.6176 A/cm$^2$, meanwhile for another sample it is 0.98 A/cm$^2$. Typical behaviour in high $T_C$ superconductor materials is the increment in $T_C$ value that promotes higher magnetic field of the material but it decreases the intra-granular $J_C$ values.

Figures 7(a) and 7(b) show the morphologies of the prepared samples using both solid-state and co-precipitation method. There were random plate-like grains arrangements for all the samples with almost identical sizes. This structure has become a signature of the Bi-2223 phase formation from the Bi-2212 matrix mostly due to the prolonged sintering process [19]. Distribution of grains in sample prepared by co-precipitation method was more homogenous and have better grain alignment of its crystallites with c-axis. In addition, the plate-like grains were aligned to make denser and conductive sample.

Figure 7. Scanning Electron Microscopy micrographs for Bi-2223 bulk samples prepared by (a) solid-state method and (b) co-precipitation method.
4. Conclusion
The co-precipitation method has proven to provide more advantages in comparison to the solid-state reaction method with regard to the process conditions and the quality of the BSCCO powder produced. Sample prepared by the co-precipitation method is homogeneous and has better superconducting quality in comparison to the time-consuming solid-state method, which needs repetition of grinding process in order to achieve the required homogeneity.

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