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Optimization for preparing Bi$_{1.68}$Pb$_{0.32}$Sr$_{1.75}$Ca$_{1.85}$Cu$_{2.85}$O$_{10+y}$ powders by wet ball milling

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Abstract

Superconducting Bi$_{1.68}$Pb$_{0.32}$Sr$_{1.75}$Ca$_{1.85}$Cu$_{2.85}$O$_{10+y}$(Bi-2223) powders were prepared by a conventional solid-state reaction using hand grinding and wet ball milling. The effects of the ball milling and sintering times on the phase evolution were examined by x-ray diffraction and magnetic susceptibility measurements. Single-phase Bi-2223 powders with a superconducting transition temperature of about 108 K were optimally prepared by wet ball milling for 20 h and sintering at 867 °C for 80 h. Finding these optimal preparation conditions were crucial for mass producing high-quality single-phase Bi-2223 precursor powders with a much lower cost of energy. Furthermore, we found that ball milling led to thinner grains than hand grinding.

1. Introduction

(Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$ (Bi-2223) high temperature superconductor (HTSC) has a great potential for a variety of applications such as power transmission cables [1, 2], superconducting magnets [3, 4], motors [5, 6], generators [7, 8], transformers [9, 10], current limiters [11, 12] and current leads [13, 14]. This is because the first generation of the Bi-2223 superconducting tapes can carry a sufficiently high transport critical current density, $J_c$, and can be mass produced with a rather low price compared with the second generation of the superconducting tapes [15]. The major challenge for producing the high- $J_c$ Bi-2223 tapes is that the Bi-2223 phase is thermodynamically unstable near and above its melting point [16]. Even in the best Bi-2223 tapes in the market, the content of the Bi-2223 phase is less than 80%. The Bi$_2$Sr$_2$CaCu$_2$O$_{8+y}$ (Bi-2212) phase with a much lower superconducting critical transition temperature ($T_c$) is frequently present in the Bi-2223 tapes [17, 18], which should be responsible for reducing $J_c$. In order to produce Bi-2223 tapes with a much higher $J_c$, it is essential to produce the tapes containing a much higher fraction of Bi-2223 phase [19]. To achieve this goal, the first step is to prepare highly pure Bi-2223 precursor powders. Indeed, our preliminary result shows that the tapes prepared with highly pure Bi-2223 precursor powders can carry a much higher $J_c$.

There are several methods to synthesize the Bi-2223 precursor powders such as solid-state reaction [20], oxalate co-precipitation [21], spray drying [22], sol-gel route [23] and spray pyrolysis [24, 25]. Among these methods, single-phase Bi-2223 precursor powders can be made by solid-state reaction using hand grinding [26]. This preparation method is difficult to scale up for mass production. Some of other methods can be scaled up, but there are more or less some impurity phases in Bi-2223 precursor powders prepared by these methods.

In contrast to the Bi-2212 phase, the Bi-2223 phase is stable in an extremely narrow temperature range of about 50 °C just below the incongruent melting line and thus synthesizing the Bi-2223 phase with acceptable purity has been a particularly difficult task, and the sluggish formation rate of the Bi-2223 phase makes the task even more arduous [27, 28]. Due to the evaporation of Bi and Pb elements at high temperatures, nominal
composition Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$ was adjusted into nominal composition Bi$_{1.68}$Pb$_{0.32}$Sr$_{1.75}$Ca$_{1.85}$Cu$_{2.85}$O$_{10+y}$ in order to obtain Bi-2223 single phase. In this work, we succeeded to make a large quantity of highly pure Bi-2223 phase precursor powders by the solid-state reaction method and ball milling. The influences of the ball milling parameters on the phase purity and on the critical transition temperature of Bi-2223 phase precursor powders were studied systematically. For comparison, we also made the Bi-2223 samples by hand grinding.

2. Materials and methods

The following procedures were used to prepare Bi-2223 samples with hand grinding. According to the nominal composition Bi$_{1.68}$Pb$_{0.32}$Sr$_{1.75}$Ca$_{1.85}$Cu$_{2.85}$O$_{10+y}$, the starting powders of Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, and CuO (respective analytical grade is 99.9%, 99.9%, 99.95%, 99.99%, 99.9%) were purchased from MacLean Reagents. The oxides and carbonates of higher purity (>99.999%) did not improve the sample quality [29]. These homogeneous mixed powders were reacted in gold crucible in air and thereafter subjected to two calcination processes for 24 h at 807 °C in NBD-M1700 high temperature box-type sintering furnace with one intermediate grinding (quenching) for the sake of producing an oxide precursor without residue of any carbonates. After completion of the calcining, specimens were left in the gold crucibles to cool down to room temperature by themselves. The prepared powders were successively ground and pressed in pellet shape under a pressure of 415 MPa. These pellets of 19 mm diameter and 2 mm thickness were annealed in gold crucibles at 867 °C for 40 h in air. The heating and cooling rates were 5 °C min$^{-1}$. This sintering process was repeated twice with intermediate grindings. These grinding steps aim to avoid any preferred orientation of grains inside the material and thus to ensure a random spatial distribution of the reflection intensity [30].

The following procedures were used to prepare Bi-2223 samples with ball milling. The raw powders of same stoichiometric ratio were ball milled using SFM-1 planetary ball milling technique in agate container and agate balls with various processing parameters. The wet ball milling was adopted with alcohol liquid. The notation and experimental variables for all precursor powders were summarized in table 1. Each time we varied ball milling time and kept both the rotation speed and the weight ratio of ball to powder to liquid constant. The process of milling was paused for 10 min every 20 min in favor of cooling the system down and reversing rotation. The following preparation procedures were the same as that of hand grinding, except for the sintering times. The sintering process was repeated once with intermediate grindings. The hand-ground and ball-milled precursor powders were labeled as P0, P1, P2, P3 and P4.

X-ray diffraction (XRD) experiment was carried out on Bi-2223 precursor powders using a Bruker D8 Advance x-ray diffractometer with Cu-K$_\alpha$ radiation in the angular range of $2\theta = 3$–90 degree at 3 deg min$^{-1}$ scanning speed and 0.02 deg scanning step. The superconducting transition temperature was determined from magnetic susceptibility measurements carried out in a cryogen-free measurement system (CFMS). A magnetic field of $\sim$ 50 Oe was applied at 140 K before cooling to 10 K (field-cooled measurement). The microstructure of the Bi-2223 precursor powders was characterized using an America-FEI-Quanta FEG 250 scanning electron microscope (SEM) at an acceleration voltage of 10 kV.

3. Results and discussion

Figure 1 (a) shows the XRD patterns of hand-ground precursor powders sintered at 867 °C for different times. There are some amounts of Bi-2201 and Bi-2212 impurity phases in hand-ground precursor powders sintered at 867 °C for 40 h. Minor Bi-2201 and Bi-2212 phases remain in hand-ground precursor powders sintered at
867 °C for 80 h. When they are sintered at 867 °C for 120 h, all diffraction peaks can be assigned to the Bi-2223 phase. This indicates a nearly complete conversion of the impurity phases into the Bi-2223 phase.

Figure 1(b) shows temperature dependences of the magnetization for the hand-ground samples sintered at 867 °C for different times. $T_c$ is defined as the diamagnetic onset temperature. From figure 1(b), it can be seen that the $T_c$ of the sample decreases as the sintering time increases from 40 h to 80 h. This decrease should be due to Pb volatilization during further sintering process. Further increase of the sintering time does not change $T_c$.

According to the XRD results and magnetic susceptibility measurements, the hand-ground precursor powders sintered for 120 h contain the Bi-2223 single-phase. Figure 2 presents SEM image of the hand-ground precursor powders sintered for 120 h. From figure 2, it can be seen that the hand-ground precursor powders have a laminar structure with a thickness of about 0.69 μm.

The effects of ball milling and sintering times on the phase purity of the Bi-2223 precursor powders are shown in figure 3. In the ball-milled precursor powders sintered at 867 °C for 40 h (figure 3(a)), there are substantial amounts of Bi-2201 and Bi-2212 phases for the ball milling time of 10 h, and minor Bi-2201 and Bi-2212 phases for the ball milling times of 20 h, 30 h and 60 h. The samples were further sintered at 867 °C for 80 h (figure 3(b)). The sample prepared with the ball milling time of 20 h contains pure Bi-2223 phase (all diffraction peaks can be assigned to the Bi-2223 phase). However, there are some amounts of Bi-2201 and Bi-2212 phases in the samples prepared with other ball milling times.

Magnetic susceptibility data of the Bi-2223 phase precursor powders prepared with different ball milling times are presented in figure 4 and table 2. It is clear that the $T_c$ of the samples sintered at 867 °C for 40 h and 80 h...
both increases as the balling time increases from 10 h to 20 h, and then decreases with further increasing the ball milling time. For the samples prepared with different ball milling times, the $T_c$ of the samples sintered at 867 °C for 40 h is overall a little higher than that for 80 h. Combining with XRD results (figure 3), we conclude that single-phase Bi-2223 precursor powders can be made by ball milling for 20 h and sintering at 867 °C for 80 h, and that the ball milling significantly reduces the sintering time (40 h) and thus lowers the energy cost compared with hand grinding. Single-phase Bi-2223 precursor powders made by ball milling for 20 h and sintering at 867 °C for 80 h show good superconducting properties with $T_c \sim 108$ K. Figure 5 shows microstructure of the single-phase Bi-2223 precursor powders made by wet ball milling for 20 h and sintering at 867 °C for 80 h. By comparing figure 5 with figure 2, it can be seen that ball milling results in much finer precursor powders (thickness of about 0.32 μm) than hand grinding (thickness of about 0.69 μm), which could result in a better orientation of the superconducting grains and a higher critical current density in the superconducting tapes [31–33]. The difference of thickness of precursor powders between ball milling and hand grinding is most likely due to grain refinement or micro-scale distortion and strain by the ball milling [34, 35].

### Table 2. $T_c$ variation with increasing ball milling time for the Bi-2223 phase precursor powders at 840 °C for different sintering times.

| Ball milling time (h) | 10  | 20  | 30  | 60  |
|----------------------|-----|-----|-----|-----|
| $T_c$ for the samples sintered at 867 °C for 40 h (°C) | 107.64 | 108.06 | 107.89 | 107.65 |
| $T_c$ for the samples sintered at 867 °C for 80 h (°C) | 107.25 | 107.48 | 107.42 | 107.24 |

Figure 3. XRD patterns of the Bi-2223 phase precursor powders prepared with different ball milling times: (a) sintered at 867 °C for 40 h; (b) sintered at 867 °C for 80 h.

Figure 4. Magnetic susceptibility data of the Bi-2223 phase precursor powders prepared with different ball milling times: (a) temperature dependences of the magnetization for the samples sintered at 867 °C for 40 h; (b) temperature dependences of the magnetization for the samples sintered at 867 °C for 80 h.
4. Conclusions

The influences of both ball milling and sintering times on the phase purity and superconducting critical transition temperature of the Bi-2223 precursor powders have been studied systematically. We find that the ball milling time of 20 h and sintering time of 80 h at 867 °C are considered to be the optimal process conditions for preparing a large quantity of single-phase Bi-2223 precursor powders. Finding these optimal preparation conditions are crucial for mass producing high-quality single-phase Bi-2223 precursor powders with a much lower cost of energy. Moreover, ball milling leads to a laminar structure with a smaller thickness, which could result in a better orientation of the superconducting grains and a higher critical current density in the superconducting tapes.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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