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ARTICLE

Comparison of Intermediate Phase Evolution in Bi-2212 Powders Prepared by Spray Pyrolysis and Co-precipitation Methods for High Performance Wires

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Abstract: $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) precursor powders were prepared by spray pyrolysis (SP) and co-precipitation (CP) processes separately. The intermediate phase evolution of Bi-2212 grains was investigated. Compared with that prepared by CP process, the phase formation rate of Bi-2212 grains prepared by SP process is obviously improved. Furthermore, the residual carbonates in CP powders hinder the formation of Bi-2212 grains, while the nitrates in SP powders only have a weak influence on the growth of Bi-2212 grains. The properties of Bi-2212 wires from SP precursor powder are close to those of the ones from CP precursor powder. Considering the much higher fabrication efficiency, SP process is useful for mass production of Bi-2212 wires.

Key words: Bi-2212; precursor powder synthesis; phase formation; spray pyrolysis

$Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) high temperature superconducting wire has attracted much attention, since it can be used as desirable isotropic and multifilament round-wire[1]. The high irreversibility field and the high current capacity under the low temperature and high field condition of Bi-2212 alloy are crucial in high field magnets and Rutherford cables[2-4]. Recently, it is reported that the Bi-2212 insert coil can generate a magnetic field of 2.6 T under the background field of 31.2 T[5], which indicates the large potential of Bi-2212 wires in the practical application. Furthermore, Kadar et al[6] studied the microstructure, phase formation, and texture evolution of monofilament and multifilament wires during the melting process. Kametani et al[7] compared the growth textures of round Bi-2212 wires and flat Bi-2223 tapes. So far obvious developments of Bi-2212 have been achieved.

The typical technique for preparing Bi-2212/Ag wires is powder-in-tube (PIT) process. There are three key steps in PIT process, including the powder preparation, mechanical deformation, and heat treatment processes[8,9]. One of them is the preparation of high quality precursor powder. The effects of precursor powder composition on the critical current (I_c) and critical current density (J_c) of Bi-2212/Ag wires or tapes were investigated by Nexans and Oxford Superconducting Technology (OST) [10]. The influence of the precursor powders with different stoichiometric ratios on the partial melt processing for Bi-2212 bulks was also analyzed[11-13]. In addition, the continuous solid-state process inside a roller furnace was used to synthesize the Bi-2212 powder[14]. Recently, the effect of precursor powder preparation techniques on the superconducting properties of Bi-2212 wires was investigated by National High Magnetic Field Laboratory (NHMFL) [15]. Three kinds of precursor powders were separately fabricated by chemical co-precipitation (CP), spray pyrolysis (SP), and solid state process. SP process is also regarded as the nanospray combustion chemical vapor condensation, namely nCCVC. Jiang et al[15] reported the results of I_c and J_c of Bi-2212 wires with the optimization of powder preparation methods. The I_c (absolute temperature of

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4.2 K, background magnetic field intensity of 5 T) of 888 A for Bi-2212 wire from nCCVC powders can be achieved, which indicates that nCCVC method is better than other traditional CP techniques for the industrial fabrication of Bi-2212 wires.

In this research, the traditional CP method and SP technique were used to prepare the Bi-2212 precursor powders. The microstructure and phase evolution of Bi-2212 powders were investigated. The comparisons between two different powders on the thermal gravimetric analysis, phase formation mechanism, and the final superconducting performance of round wires were conducted.

1 Experiment

The Bi-2212 precursor powders with the mass ratio of Bi: Sr: Ca: Cu=2.17: 1.94: 0.89: 2.00 were synthesized with Bi_2O_3, $SrCO_3$, $CaCO_3$, and Cu as raw materials through SP and CP processes, separately. All the raw materials reacted with the nitric acid to form precursor nitrate solutions of $Bi(NO)_3$, $Sr(NO_3)_2$, $Ca(NO_3)_2$, and $Cu(NO_3)_2$. During SP process, the nitrate solutions were directly sprayed into the pyrolysis chamber to acquire the SP precursor powder[16,17]. The SP precursor powder was sintered in air at 640, 820, and 850 °C for 10, 20, and 20 h, respectively, and then moderately ground to obtain the final Bi-2212 SP precursor powder.

In CP process[18,19], the nitrate solution was firstly mixed with the oxalic acid precipitant. Secondly, the precipitate was pyrolyzed at 500 °C for 8 h to obtain the precursor powder. The CP precursor powder was sintered in air at 640, 740, 800, 820, and 850 °C for 10, 10, 10, 20, 20 h, respectively, and then moderately ground to obtain the final Bi-2212 CP precursor powder.

Bi-2212 multi-filament wires were fabricated by PIT process with two crystallized powders. The Bi-2212 powder in the wire was surrounded by the inner sheath of Ag and outer sheath of AgMn alloys. The wires with 37×18 filaments were made with a series of swaging, drawing, and re-bundling processes. A typical overpressure heat treatment was performed to obtain the wires with high performance[9,20].

Thermal gravimetric analysis (TA Q1000DSC) of precursor powder was performed with the heating rate of 20 K/min in air. The phase components of the powder sintered at different temperatures were investigated by X-ray diffraction (XRD) using Cu Kα radiation (Bruker D8 Advance). The morphology of powder was characterized by scanning electron microscopy (SEM, JSM-6700). The cross-section morphology of the wire was investigated by optical microscopy (OM, Olympus PMG3). Critical currents of sintered Bi-2212 wires were measured using the four-probe method with the criterion of 1 μV/cm at absolute temperature of 4.2 K.

2 Results and Discussion

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used to study the phase evolution of SP and CP precursor powders. Fig. 1 shows the TG and DSC curves of the two pyrolyzed powders. There is an obvious mass loss (~23%) in the temperature range of 250~620 °C for the SP powder (Fig. 1a). Then there is a very weak mass loss (about 1%) when the temperature is close to 880 °C. TG curve of CP powder shows a large mass loss (~13.8%) in the temperature range of 550~820 °C (Fig. 1b).

The variation of DSC curves can be attributed to different phase formation reactions. DSC curve of SP powder displays three endothermic peaks at 541, 618, and 880 °C, which is associated with the obvious mass loss of TG curve. The endothermic peaks at 541 and 618 °C can be attributed to the decomposition of the nitrate residues and the formation of $Bi_2Sr_2CuO_{6+\delta}$ (Bi-2201) in the SP powders. The endothermic peak at 880 °C may be ascribed to the melting point of Bi-2212 SP powder under air atmosphere (Fig. 1a). In addition, DSC curve of CP powder shows weak endothermic peaks at 620, 719, 788, 820, and 840 °C. The endothermic peaks at 620 and 719 °C can be ascribed to the decomposition of carbonates and the formation of Bi-2201-CP intermediate phase; the endothermic peaks at 788, 820, and 840 °C may be ascribed to the complex formation of Bi-2212 phase of CP powder (Fig. 1b). The obviously different TG and DSC curves indicate the diverse crystallization behavior of the two precursor powders. The crystallization reaction temperature of SP powder is clearly lower than that of CP powder, which may promote the phase formation of Bi-2212 phase.

The phase evolutions of the two powders were investigated

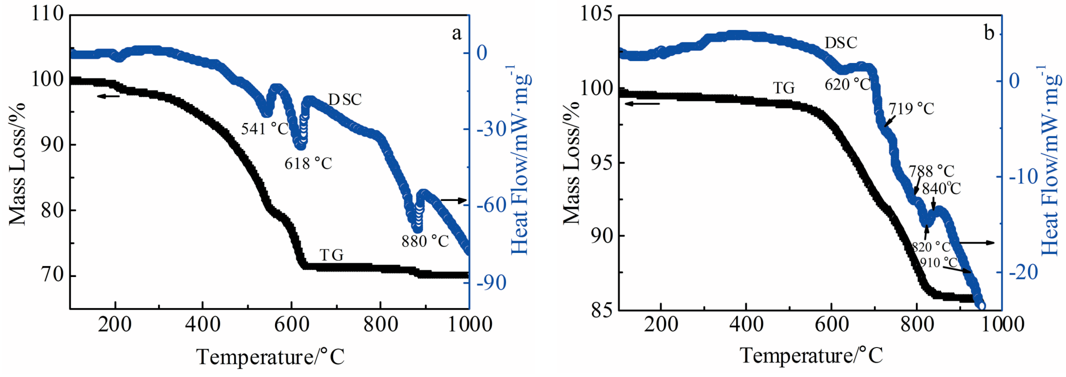

Fig.1 TG and DSC curves of SP (a) and CP (b) precursor powders

by XRD. Fig.2 shows the θ-2θ scanning results of SP powders sintered at temperatures of 640, 820, and 850 °C. The original SP powder is composed of $Ca_{0.33}Sr_{0.67}(NO_3)_2$, $Sr_xBi_{1-x}O_y$ (x=0.2~0.3), and CuO, which indicates that the decomposition reactions of $Bi(NO_3)_3$ and $Cu(NO_3)_2$ begin earlier than those of $Ca(NO_3)_2$ and $Sr(NO_3)_2$ do. The residual Ca/Sr-nitrates may affect the formation of intermediate phases, which is consistent with the TG and DSC curves in Fig.1a. At 640 °C, the SP powder consists of the main phase of Bi-2201 and the other minor phases of CaO, CuO, SrO, and $Sr_xBi_{1-x}O_y$. The decomposition of $Ca_{0.33}Sr_{0.67}(NO_3)_2$ is accompanied with the formation of Bi-2201 phase, as indicated by the (113) peak at 2θ=25.9°. The related reactions are presented by Eq.(1) and Eq.(2), as follows:

$$Sr_xBi_{1-x}O_y+CuO \rightarrow Bi_2Sr_2CuO_{6+\delta} \tag{1}$$

$$3Ca_{0.33}Sr_{0.67}(NO_3)_2 \rightarrow CaO+2SrO+6NO_2 \tag{2}$$

When the temperature is above 820 °C, there is only Bi-2212 phase, as identified by the (115) peak at 2θ=27.48°. Besides, the Bi-4413 phase in the powders at 850 °C cannot be observed[21]. The chemical reaction can be concluded by Eq.(3), as follows:

$$Bi_2Sr_2CuO_{6+\delta}+CaO+CuO \rightarrow Bi_2Sr_2CaCu_2O_{8+\delta} \tag{3}$$

For the CP powder, $CaCO_3$, Bi_2O_3, $SrCO_3$, $Sr_xBi_{1-x}O_y$, CaO, and CuO can be observed in Fig. 3, indicating the decomposition of oxalates. With increasing the temperature, $Bi_{0.8}Sr_{0.1}Ca_{0.1}O_{1.4}$, $CaBi_2O_4$, and $Sr_xBi_{1-x}O_y$ can be observed in CP powder sintered at 640 °C[17,18]. Other phases, such as $CaCO_3$, $SrCO_3$, and CuO, can also be observed in Fig. 3, implying the reactions between the oxides and carbonates. The corresponding reactions can be concluded by Eq.(4~6), as follows:

$$Bi_2O_3+SrCO_3 \rightarrow Sr_xBi_{1-x}O_y+CO_2 \tag{4}$$

$$Bi_2O_3+CaCO_3 \rightarrow CaBi_2O_4+CO_2 \tag{5}$$

$$4Bi_2O_3+SrCO_3+CaCO_3 \rightarrow 10Bi_{0.8}Sr_{0.1}Ca_{0.1}O_{1.4}+2CO_2 \tag{6}$$

At 740 °C, the major phase of Bi-2201 appears with a few residues of $SrCO_3$, $CaCO_3$, and CuO, suggesting the decomposition of carbonates and the formation of Bi-2201 phase. The corresponding reactions can be concluded by Eq.(7~9), as follows:

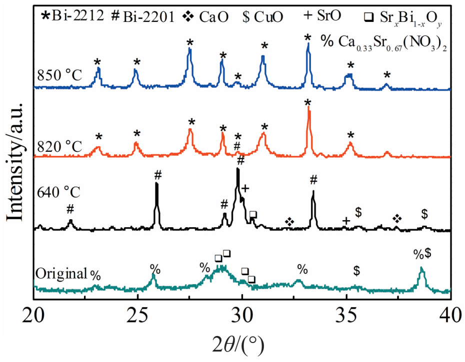

Fig.2 XRD patterns of SP precursor powders sintered at different temperatures

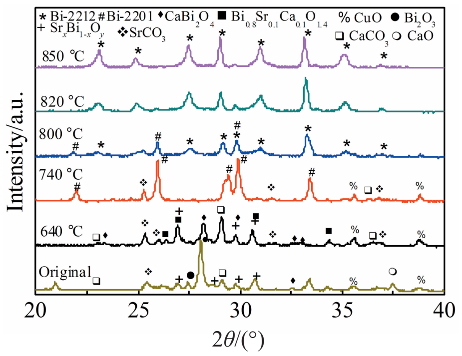

Fig.3 XRD patterns of CP precursor powders sintered at different temperatures

$$Sr_xBi_{1-x}O_y+CuO \rightarrow Bi_2Sr_2CuO_{6+\delta} \tag{7}$$

$$SrCO_3 \rightarrow SrO+CO_2 \tag{8}$$

$$CaCO_3 \rightarrow CaO+CO_2 \tag{9}$$

The phase evolution of CP powder according to XRD patterns is in accordance with the results of TG and DSC curves. When the sintering temperature is 800 °C, the main phases are Bi-2212 and Bi-2201 phases. Bi-2212 phase can be acquired at 850 °C. The chemical reaction is represented by Eq.(10), as follows:

$$Bi_2Sr_2CuO_{6+\delta}+CaO+CuO \rightarrow Bi_2Sr_2CaCu_2O_{8+\delta} \tag{10}$$

In order to compare the formation rate of SP and CP powders, the intensities of (115) and (113) peaks of Bi-2212 and Bi-2201 phases are plotted as a function of temperature in Fig. 4, respectively. For the two precursor powders, the intensity of (113) peak of Bi-2201 phase is increased firstly and then decreased with increasing the temperature. The intensity of (115) peak of Bi-2212 phase is increased in the temperature range of 640~850 °C. The intensity of (113) peak of Bi-2201 phase reaches the maximum at 640 and 740 °C for SP and CP powders, respectively, which proves the high reaction activity of SP powders. Meanwhile, the intensity of (115) peak of Bi-2212 phase in SP powder increases faster than that in CP powder does. The formation of Bi-2212 phase in SP powder begins at 640 °C, while that in CP powder starts

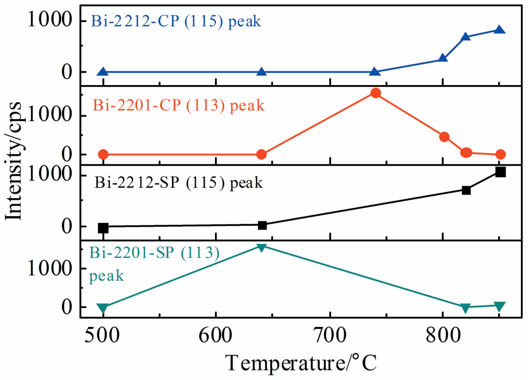

Fig.4 Intensities of (113) peak of Bi-2201 phase and (115) peak of Bi-2212 phase of SP and CP powders

at 740 °C. At 820 °C, the full width at half maximum (FWHM) value of (115) peak of Bi-2212 phase in SP powder (0.23°) is smaller than that in CP powder (0.35°), indicating a sharper peak of SP powder and a faster grain growth in SP powder. At the final crystallization temperature of 850 °C, the FWHM of (115) peak of Bi-2212 phase in SP powder (0.22°) is close to that in CP powder (0.25°). The sharp peak shows the good crystalline of Bi-2212 phase. Furthermore, according to XRD results, all phases are converted into Bi-2212 phase. The purity of Bi-2212 phase is about 99% in final crystallized SP and CP powders. Based on the above analyses, the SP powder can lead to the decrease of phase formation temperature of Bi-2201 and Bi-2212 phases. Thus, the calcination process can be simplified and the preparation efficiency of Bi-2212 phase is improved.

Different reaction pathways of Bi-2212 phase are derived from the change of intermediate phases. The decomposition temperature of $CaCO_3$ (T=825 °C) is higher than that of $Ca(NO_3)_2$ (T=561 °C); the decomposition temperature of $SrCO_3$ (T=1100 °C) is much higher than that of $Sr(NO_3)_2$ (T= 570 °C)[22]. It can be concluded that the decomposition temperature of carbonates is obviously higher than that of nitrates. The residual carbonates may result in the higher formation temperature of Bi-2212 phase. Hence, the CP powder may need more heat treatments with intermediate grinding to prohibit the carbonates residues. The nitrates in SP powder may lead to the acute reaction, which is beneficial for the formation of Bi-2212 phase.

Fig.5 and Fig.6 show the SEM morphologies of SP and CP powders sintered at different temperatures, respectively. Hollow sphere particles can be observed in Fig.5a, which is the typical morphology of original SP powder. The size of particle is 1~3 μm. Some soft hollow particles are composed of minor needle-like grains. At 640 °C, the original sphere particles are broken into the mixture of fine needle-like grains and plate-like grains, as shown in Fig.5b. With increasing the temperature, the needle-like grains disappear and the plate-like grains become bigger and thicker with the size of grains of 3~5 μm (Fig.5c and 5d).

The morphology evolution of CP powder is obviously different. Non-crystal agglomeration can be observed in Fig.6a, resulting from the decomposition of the oxalate. With increasing the temperature, the soft agglomeration crystallizes step by step. Some irregular and plate-like grains appear at 740 °C, and the grains grow bigger (Fig. 6b and 6c). The irregular grains are gradually transformed into the lamellar grains with further increasing the temperature. It is confirmed that the large lamellar grains correspond to the Bi-2212 grains. The size of Bi-2212 grains in CP powder is close to that in SP powder. The morphology evolution of powders agrees with the XRD results.

Two kinds of Bi-2212 powders were fabricated into multi-filament wires and characterized by final performance. Fig.7 shows the critical currents of Bi-2212 wires from SP and CP powders at absolute temperature of 4.2 K under self-field. The value of I_c is 885.6 and 968.4 A for Bi-2212 wires from SP and CP powders, respectively. The uniformity of Bi-2212 filaments from SP powders is similar to that from CP powders, as indicated by the insets in Fig.7. The number of filaments in the wire was set as 666. The diameter of wire was 1.0 mm. The value of J_e is 1128 and 1233 A/mm^2 for the Bi-2212 filaments from SP and CP powders, respectively. In comparison with the results in Ref.[9, 20], both wires show good performance. Although the performance of Bi-2212 from SP powder is slightly worse than that from CP powder, the Bi-2212 from SP powder still matches the requirement of high performance of Bi-2212/Ag wires. Further optimization of the heat treatment parameters may enhance the

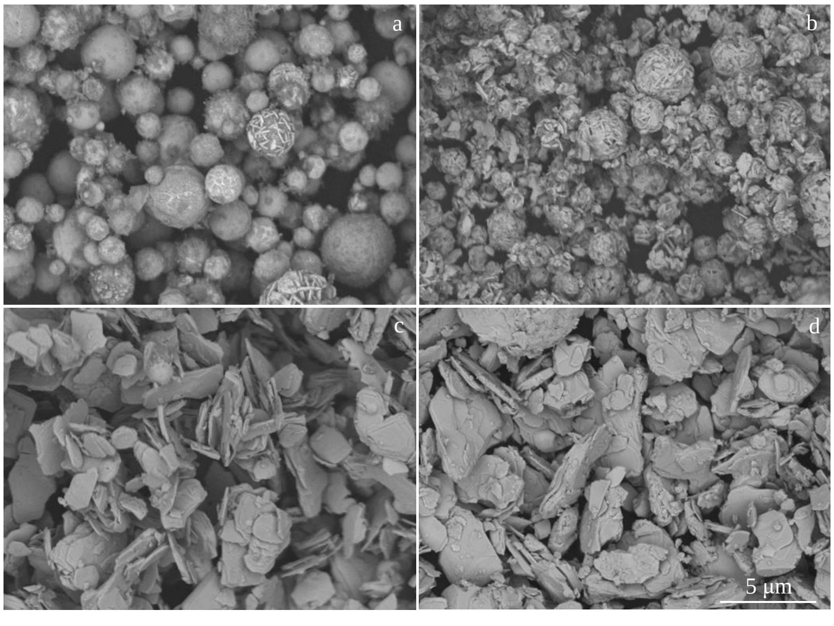

Fig.5 SEM morphologies of SP precursor powders sintered at different temperatures: (a) original, (b) 640 °C, (c) 820 °C, and (d) 850 °C

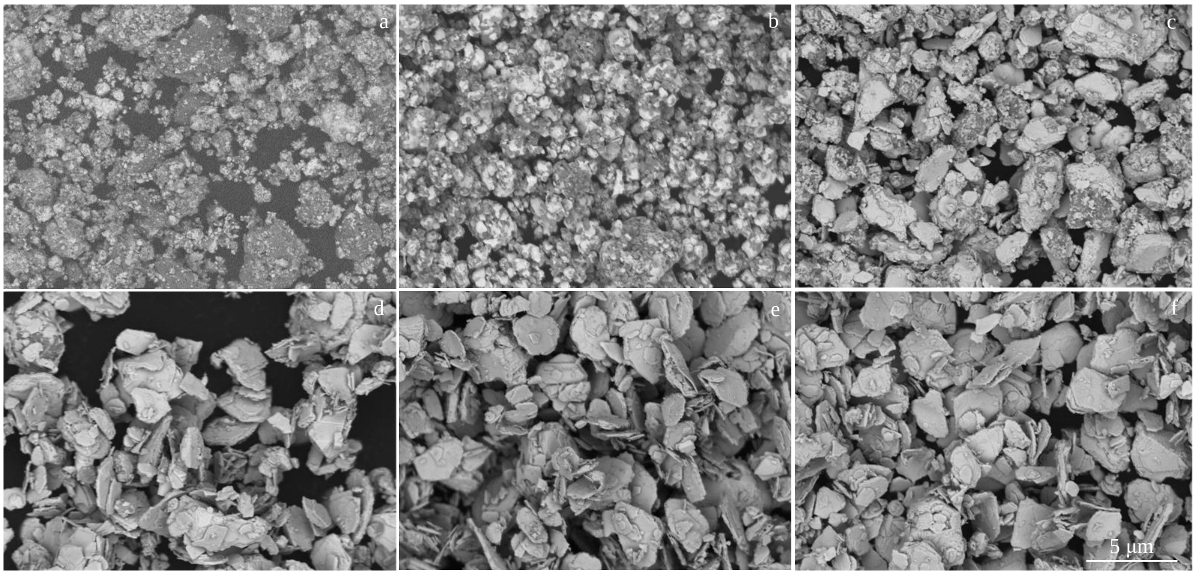

Fig.6 SEM morphologies of CP precursor powders sintered at different temperatures: (a) original, (b) 640 °C, (c) 740 °C, (d) 800 °C, (e) 820 °C, and (f) 850 °C

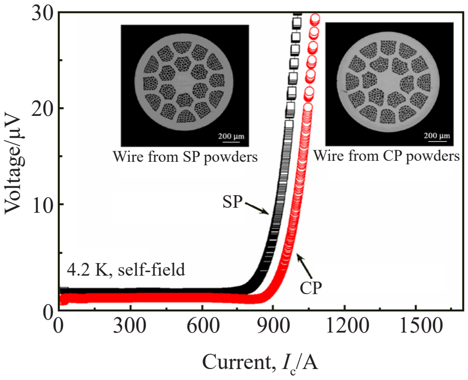

Fig.7 Voltage-current curves of Bi-2212 wires from SP and CP powders (insets are OM images of cross-sectional morphologies of Bi-2212 wires from SP and CP powders)

performance of wire with SP powder.

3 Conclusions

1) The formation rate of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) phase in spray pyrolysis (SP) powder is much higher than that in co-precipitation (CP) powder. The starting crystallization temperature of SP powder is clearly lower than that of CP powder.

2) During the sintering process, the residual of Ca/Sr-carbonates in CP powder is the critical hindrance to the phase formation of Bi-2212 phase. Hence, the CP powders need more heat treatment steps including intermediate grinding for the sufficient reaction of the intermediate phases. While the residual Sr/Ca-nitrates in SP powder have a weak influence on the sequent growth of Bi-2212 grains.

3) The Bi-2212 phase in SP powder forms easily at low temperature. The reaction process is simplified and better fabrication efficiency of high purity Bi-2212 SP powder can be achieved. Further optimization of the heat treatment parameters for preparation of Bi-2212 wires with SP powder can enhance the performance of wires. Therefore, SP powder is beneficial for the mass production of Bi-2212 wires.

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喷雾热解与共沉淀法制备高性能线材用Bi-2212粉末的中间相演变对比研究

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摘　要：采用喷雾热解和共沉淀工艺分别制备了$Bi_2Sr_2CaCu_2O_{8+\delta}$(Bi-2212)前驱粉末，研究了Bi-2212前驱粉的中间相演化过程。与共沉淀工艺相比较，喷雾热解工艺提高了前驱粉末中Bi-2212晶粒的相转变效率；而且喷雾热解后粉末中残留的硝酸盐对Bi-2212晶粒的生长影响较小，共沉淀后粉末中残留碳酸盐会阻碍Bi-2212晶粒的形成。采用喷雾热解法制备的Bi-2212线材的性能与采用传统共沉淀工艺法制备的线材性能相近，但喷雾热解工艺的制备效率更高。因此，采用喷雾热解制备前驱粉末有助于实现Bi-2212线材的大规模生产。

关键词：Bi-2212；前驱粉末合成；相形成；喷雾热解

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