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Heat treatment on phase evolution of Bi-2223 precursor powder prepared by spray pyrolysis method*

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The phase evolution of Bi-2223 precursor powder prepared by spray pyrolysis method is studied with different heat treatment parameters. The results show that the reaction temperature and phase composition of precursor powder depend on heat treatment atmosphere. Phase assemblage of (Bi,Pb)-2212, AEC, CuO, and small Bi-2201 can be obtained by heat-treated in N_2-0.1%O_2 atmosphere. For precursor powder, there is sufficient reaction process at 770 °C, and the dimension of Bi-2212 phase increases rapidly with the increase of heat treatment temperature and time. The dimension of AEC phase also increases by extending heat treatment time. As a balance among phase assemblage, dimension of particle and adequate reaction, a reasonable precursor powder can be obtained by heat-treated at 770 °C for 12 h–16 h in N_2-0.1%O_2 atmosphere. Critical current of 37-filament Bi-2223 tape is about 120 A, which confirms that these heat treatment parameters are reasonable.

Keywords: Bi-2223, phase evolution, heat treatment, spray pyrolysis

PACS: 74.25.F–, 74.25.Sv, 74.62.Bf **DOI:** 10.1088/1674-1056/28/4/047401

1. Introduction

Since the discovery of superconductivity at 30 K in the $(La,Ba)_2CuO_4$ by Bednorz and Muller,[1] many efforts have been devoted to the development of new high temperature superconductors and their applications in many different fields. $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) and $YBa_2Cu_3O_7$ (YBCO) have become the most potential high temperature superconductors for practical application up to present, and Bi-2223 has been successfully developed into product by several companies, such as SEI, AMSC, EAS, *etc.*[2–4] Bi-2223 tape is fabricated by powder-in-tube (PIT) technique. Precursor powder, mechanical deformation and heat treatment are believed to be three key factors contributed to final superconducting of Bi-2223 tape. Several different preparation methods have been reported to acquire precursor powder, including solid-state reaction, oxalate co-precipitation, spray drying and spray pyrolysis.[5–7] From the viewpoint of commercialization, a reasonable preparation method should have characteristics of simple operation, good stability, high homogeneity, large quantity and good reproducibility, and spray pyrolysis is considered to be an optimal method for the industrial preparation of Bi-2223 precursor powder.

There are many studies on precursor powder in early reports. Dorris *et al.* and Li *et al.* studied the effect of two-powder process on the phase assemblage and superconducting via co-precipitation method.[8,9] Mark *et al.* studied the effect of phase composition of precursor powder on Bi-2223 formation via spray drying method.[10] Jiang *et al.* reported the calcinations of precursor powder via solid state reaction method.[11] However, there are few studies of the phase evolution and microstructure evolution of Bi-2223 precursor powder prepared by the spray pyrolysis method.

In this work, Bi-2223 precursor powder is prepared by the spray pyrolysis method, and effects of heat treatment on phase evolution and microstructure of precursor powder are studied systematically.

2. Experiment

We prepared precursor powder, corresponding to a nominal cation composition of $Bi_{1.8}Pb_{0.34}Sr_{1.9}Ca_{2.1}Cu_{3.06}$, by the spray pyrolysis method. First, the powders were heat-treated in air and N_2-0.1%O_2 atmosphere separately to confirm phase forming temperature and study phase composition. Second, the powders were heat-treated at 730 °C/6 h, 750 °C/6, 770 °C/6 h, and 790 °C/6 h in N_2-0.1%O_2 atmosphere to study the effect of heat treatment temperature on phase composition

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and microstructure. Third, the powders were heat-treated at 770 °C for different times to study the effect of heat treatment time on phase composition and microstructure. Pellets of precursor powders were pressed at 20 MPa to anatomize the evolution of non-superconducting phases. Finally, 37-filament Bi-2223 tape is fabricated to confirm the reasonableness of heat treatment parameters.

The phase compositions were determined by x-ray diffraction (XRD). The morphology of powders was analyzed by scanning electron microscope (SEM). Magnetization measurements were performed using a physical property measurement system (PPMS, Quantum Design), and critical current (I_c) of tape was measured by the standard four-lead technique in nitrogen liquid with a 1-μV/cm electric field criterion.

3. Results and discussion

Figure 1(a) shows the heat-flow versus temperature curves of precursor powders prepared by spray pyrolysis method, which are measured at a heating rate of 2 °C/min in following air and N_2-0.1%O_2 atmosphere, respectively. It can be seen that the precursor powders have similar reaction processes in both of these two atmospheres, but the reaction temperature in N_2-0.1%O_2 is lower than in air atmosphere. The peaks between 500 °C and 700 °C are presumed to be the decomposition of some nitrates and the reactions of different compounds. The arrowed peaks are believed to be Bi-2212 formation temperature. The Bi-2212 formation temperature is about 752 °C in N_2-0.1%O_2, but it increases to 798 °C in air. When temperature is over 800 °C, the endothermic peaks are supposed to be the decomposition of Bi-2223 phase.[5]

Besides the reaction temperature, the heat treatment atmosphere affects the phase composition as shown in Fig. 1(b). The precursor powder is composed of Bi-2212, Ca_2PbO_4, AEC ($(Sr,Ca)_xCu_yO_\delta$), CuO, and some amount of Bi-2201 when it is heat-treated in air. However, when heat treatment atmosphere is changed to N_2-0.1%O_2, the Ca_2PbO_4 (CP) phase disappears and Pb is doped into Bi-2212 phase to form (Bi,Pb)-2212, corresponding to the change of Bi-2212 phase structure from tetragonal to orthorhombic structure, which can be identified by the splitting of peak at 33.2° as shown in enlarged view in the inset of Fig. 1(b). The content of Bi-2201 phase in N_2-0.1%O_2 is less than in air. As is well known, the Bi-2201 phase is not beneficial to obtaining the high critical current for Bi-2223 tape.[12] There are more AEC and CuO phases in N_2-0.1%O_2 than in air. Müller *et al.* found that keeping Pb doped into Bi-2212 phase is favorable for grain growth and significant texturing.[13] Therefore, we systematically carry out studies of heat treatment on phase evolution and microstructure of precursor powder in N_2-0.1%O_2 atmosphere.

Based on the results shown in Fig. 1, we heat-treated the precursor powders at different temperatures to confirm optimal phase forming temperature. Figure 2(a) shows the XRD patterns of precursor powders under different heat treatment temperatures in N_2-0.1%O_2 atmosphere. All of the powders are composed of (Bi,Pb)-2212, AEC, CuO, and some Bi-2201 phases. When the temperature is below 770 °C, there are some CaO phases, which means insufficient reaction. But CaO phase disappears above 770 °C, which can be attributed to sufficient reaction. With the increase of temperature, the content of CuO phase decreases obviously, but AEC phase increases. However, when temperature reaches to 790 °C, there appear some hard particles in precursor powders which is not beneficial to the process and superconductivity of Bi-2223 tape. Figure 2(b) shows the enlarged view of splitting peak at 33.2°. It can be seen that the peak is shifted toward small angle direction with the increase of temperature, which also means more sufficient reaction and effective doping of Pb into the Bi-2212 phase. It is clear that a sufficient reaction process mainly depends on the heat treatment temperature.

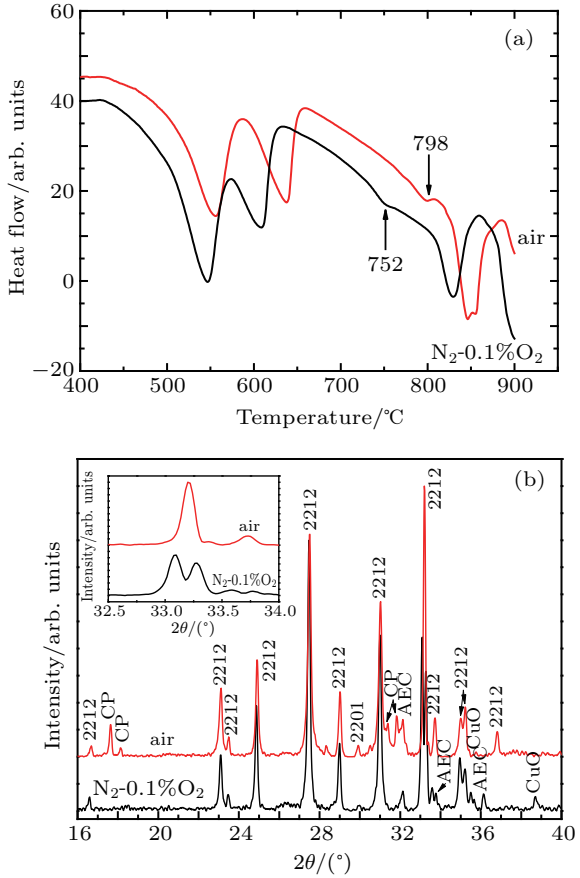


Fig. 1. (a) Curves of heat flow *versus* temperature for precursor powders at heating rate of 2 °C/min in following air (red) and N_2-0.1%O_2 (black); (b) x-ray diffraction patterns of precursor powders after heat treatment at 770 °C/6 h in air (red) and N_2-0.1%O_2 atmosphere (black) (2212:Bi-2212, 2201:Bi-2201), CP:Ca_2PbO_4, AEC: $(Sr,Ca)_xCu_yO_\delta$.

Table 1 shows the lattice parameters and full width at half maximum (FWHM) values of (0012) reflection of (Bi,Pb)-2212 phase of precursor powders heat treated at different temperatures. Both lattice parameter c and FWHM values decrease with the increase of temperature, which means sufficient reaction and effective doping of Pb into Bi-2212 phase. Considering hard particles formed at 790 °C, it seems that a reasonable temperature should be 770 °C.

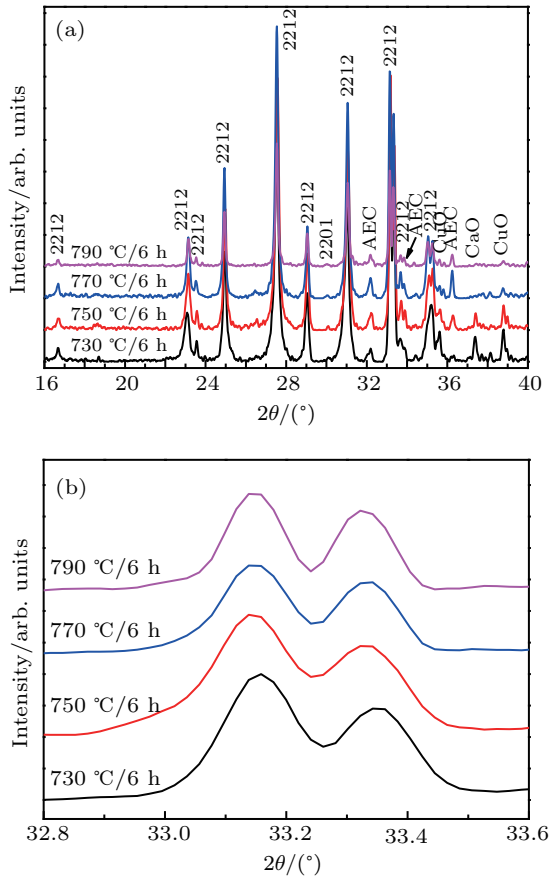


Fig. 2. X-ray diffraction patterns of precursor powders (a) heat-treated at 730 °C/6 h, 750 °C/6 h, 770 °C/6 h, 790 °C/6 h in N_2-0.1%O_2 atmosphere, and (b) an enlarged view of splitting of peaks at 33.2°.

Table 1. Lattice parameters and FWHM values of (0012) reflection of (Bi,Pb)-2212 phase in precursor powder heat-treated at different temperatures in N_2-0.1%O_2 atmosphere.

	730 °C/6 h	750 °C/6 h	770 °C/6 h	790 °C/6 h
a/Å	5.39327	5.39371	5.395	5.39587
c/Å	30.83735	30.83339	30.80376	30.73768
FWHM	0.277	0.247	0.198	0.163

Figure 3 shows the SEM micrographs of precursor powders heat-treated at different temperatures. It is obvious that all powders are composed of micaceous grains corresponding to (Bi,Pb)-2212 phase, and these micaceous grains become bigger with the increase of heat treatment temperature, which is consistent with the results of Fig. 2 and Table 1. Attributed to high activity of powder prepared by spray pyrolysis method, heat treatment process takes a short time, and the maximal dimension of micaceous grains is still less than 3 μm. Because of the long heat treatment time of powder prepared by co-precipitation or other methods, the dimension usually reaches 5 μm, or even above it.

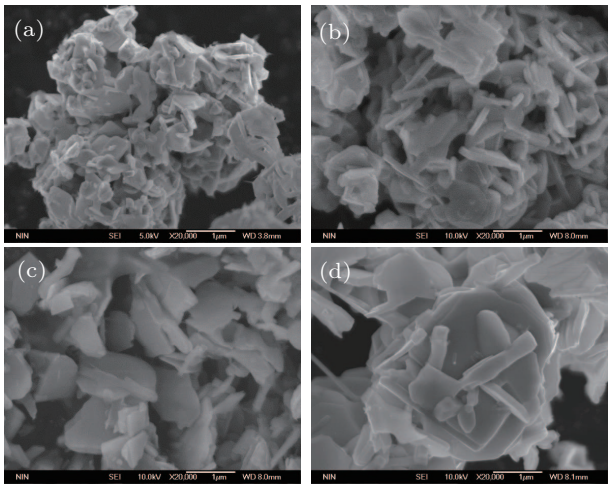


Fig. 3. SEM micrographs of precursor powders heat-treated in N_2-0.1%O_2 atmosphere at different temperatures: (a) 730 °C/6 h, (b) 750 °C/6 h, (c) 770 °C/6 h, and (d) 790 °C/6 h.

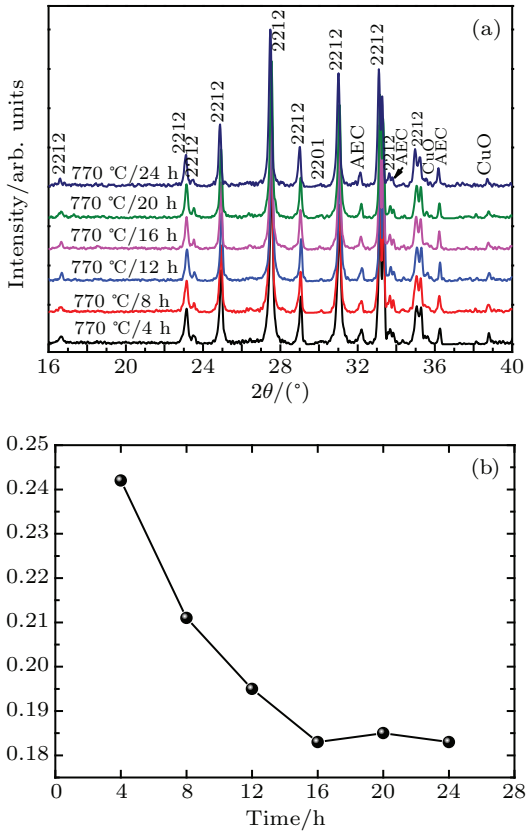


Fig. 4. (a) X-ray diffraction patterns of precursor powders heat-treated at 770 °C for 4 h, 8 h, 12 h, 16 h, 20 h, and 24 h in N_2-0.1%O_2 atmosphere; (b) FWHM value of (Bi, Pb)-2212 phase (0012) as a function of heat treatment time.

To further illuminate the effect of heat treatment time on precursor powder, the precursor powders are heat-treated at 770 °C for 4 h, 8 h, 12 h, 16 h, 20 h, and 24 h respectively.

Figure 4(a) shows the XRD patterns of precursor powders in different heat treatment times. There is no obvious difference among these precursor powders, so we think that it might just affect whether the reaction is sufficient. The variety of FWHM values, corresponding to (0012) reflection of (Bi,Pb)-2212 phase, is shown in Fig. 4(b). When heat treatment time is less than 16 h, the value of FWHM monotonically decreases. However, it has a steady trend when heat treatment time exceeds 16 h.

As shown in Fig. 5, SEM micrographs mainly show variety of dimension of (Bi,Pb)-2212 phase. When heat treatment time increases from 4 h to 12 h, the dimension of (Bi,Pb)-2212 phase grows up obviously. However, the change of dimension of (Bi,Pb)-2212 phase is not obvious when heat treatment time increases further. Besides (Bi,Pb)-2212 phase, there are some non-superconducting phases in precursor powders, such as AEC, CuO, and Bi-2201. To observe the effect of heat treatment time on non-superconducting phase, the precursor powders are pressed into pellets, which are polished carefully and observed by SEM as shown in Fig. 6. It can be seen that the dimension of AEC phase increases with the increase of heat treatment time. For a heat treatment time of 4 h, the average dimension of AEC is less than 0.3 μm, but it reaches about 1um when heat treatment time increases to 24 h. This increase of the dimension can result in the segregation of elements.

Figure 7 shows the moment-temperature curves of precursor powders heat-treated at different times. The precursor powders have almost the same superconducting transition temperatures, which mainly depends on content of oxygen. However, the content of (Bi,Pb)-2212 phase increases with the increase of heat treatment time. Unlike the results of Fig. 4(b), we cannot see a saturated tendency with the increase of heat treatment time.

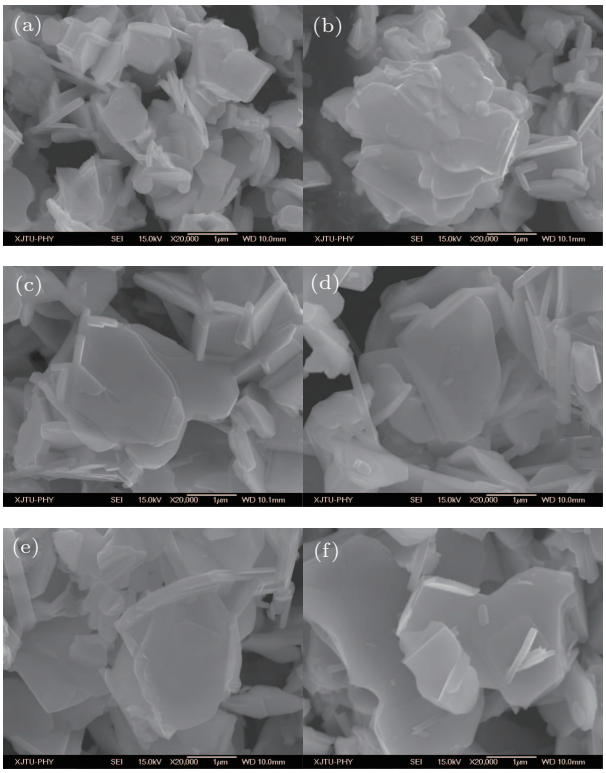


Fig. 5. SEM micrographs of precursor powders heat-treated at 770 °C in N_2-0.1%O_2 atmosphere for different times: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h, (e) 20 h, (f) 24 h.

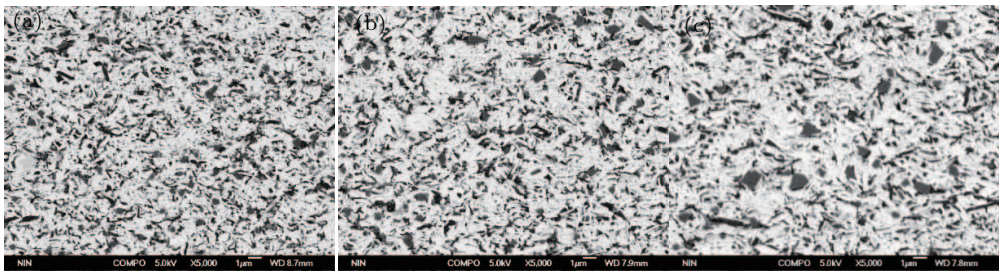


Fig. 6. SEM micrographs of pellets pressed by precursor powders heat-treated at 770 °C for (a) 4 h, (b) 12 h, and (c) 24 h in N_2-0.1%O_2 atmosphere.

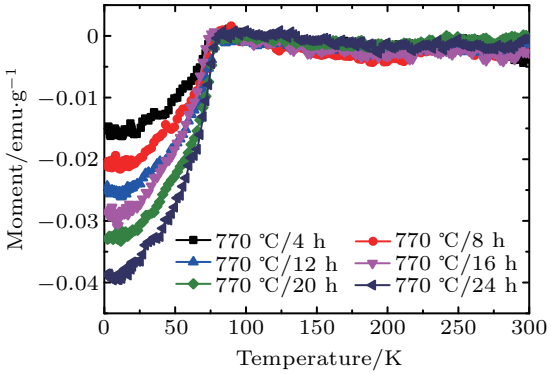


Fig. 7. Plots of zero field cooled DC magnetization *versus* heat treatment time by PPMS in 0.5-mT field.

Considering these results, we believe that a reasonable heat treatment process should be a balance between superconducting phase and non-superconducting phase. So it should be reasonable that precursor powder is heat-treated at 770 °C for 12 h–16 h in N_2-0.1%O_2 atmosphere. To confirm this viewpoint, the precursor powder is heat-treated at 770 °C/12 h in N_2-0.1%O_2 atmosphere and 37-filament tape is fabricated by the PIT method. The tape is heat-treated as reported elsewhere.[14] Figure 8 shows the *I*–*V* curve of 37-filament tape, which is measured at liquid nitrogen temperature. It can be seen that critical current is about 120 A in self-field,

which is comparable to the value for Bi-2223 tape heat-treated without over-pressure heat treatment.[7] The inset of Fig. 8 exhibits a good (00*l*) preferential orientation, and there are some non-superconducting phases formed during the post-annealing stage. The results also confirm that our heat treatment parameters are reasonable.

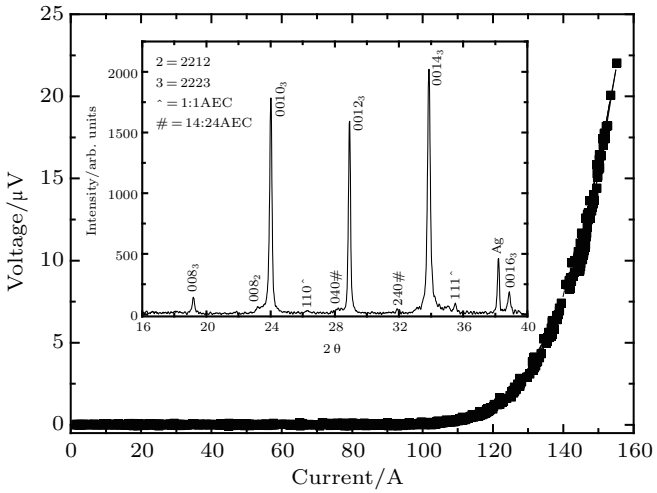


Fig. 8. The *I*–*V* curve of 37-filament tape with precursor powder heat-treated at 770 °C for 12 h in N_2-0.1%O_2 atmosphere; with inset showing x-ray diffraction pattern of 37-filament Bi-2223 tape.

4. Conclusions

We have investigated the phase evolution of Bi-2223 precursor powder with different heat treatment parameters. The main conclusions are as follows:

(i) The heat treatment atmosphere affects reaction temperature and phase composition of precursor powder. Phase assemblage of (Bi,Pb)-2212, AEC, CuO, and small Bi-2201 can be obtained by heat treatment in N_2-0.1%O_2 atmosphere.

(ii) With the increase of temperature, the reaction process tends to be more sufficient and the dimension of (Bi,Pb)-2212 particle size increases rapidly. The reasonable reaction temperature is believed to be 770 °C.

(iii) With the increase of heat treatment time, the difference in phase composition becomes not obvious but the dimension of (Bi,Pb)-2212 grows up obviously when heat treatment increases from 4 h to 12 h. This trend becomes less obvious for heat treatment time longer than 12 h. However, AEC phases increases rapidly with the increase of heat treatment time. It seems that the reaction process is sufficient when heat treatment time reaches to 12 h.

(iv) It should be reasonable that the precursor powder is heat-treated at 770 °C for 12 h–16 h in N_2-0.1%O_2 atmosphere. The critical current of about 120 A also confirms this viewpoint.

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