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ARTICLE

Influence of Cu Content in Precursor Powders on the Phase Evolution and Superconducting Properties of Bi-2212 Superconductors

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Abstract: Precursor powders of $Bi_{2.1}Sr_{1.96}CaCu_xO_{8+\delta}$(Bi-2212) high temperature superconductors with different nominal Cu ratios of x=2.0, 2.1, 2.2, 2.4 were fabricated by a modified co-precipitation process. The influences of Cu ratios on the phase evolution process during sintering were investigated. Bi-2212 thick films and single filament tapes were fabricated with dip-coating process and powder in tube process, respectively. Obvious influences of Cu ratios on the phase compositions, microstructures and superconducting properties were discussed. Results show that the initial Cu ratio can affect the thermodynamic properties of Bi-2212 phase, thus changing phase evolution process. With the increase of Cu ratio, the phase content of Bi-2201 decreases, while the content of AEC phase increases. The maximum critical current density is obtained in the x=2.2 film and tape simultaneously due to the proper phase composition and better texture structures.

Key words: high temperature superconductor; Bi-2212; nonstoichiometry; critical current density

Bi-based superconductors are of great importance for the practical applications as the high temperature superconductors (HTS)[1-4]. Because of the relatively high H_{c2} of Bi-2212 (> 100 T), and the large current capacity under high magnetic field[5], Bi-2212 insert coils have been considered to be a necessary part for the manufacturing of high field (~30 T) magnet[6-8]. However, two factors still limit the current capacity of Bi-2212 based superconductors. One is the weak pinning properties, which are mainly due to its intrinsic lattice structure[9]. Therefore, the introduction of pinning centers and modification of lattice structures can effectively enhance the flux pinning properties[10-12]. The other factor is the intergrain weak links due to the low texture degree [13-15], high porosity[16,17] and/or grain boundaries with secondary phases or amorphous layers[18,19]. Therefore, Bi-2212 with high superconducting phase content, higher texture structures and high density is necessary to obtain transport properties.

Partial melting process is an important sintering procedure for the crystallization and orientation growth of Bi-2212 grains. The decomposition of Bi-2212 during the melting process leads to the appearance of secondary phases, such as Bi-2201 ($Bi_2Sr_2CuO_{6+\delta}$) and AEC (alkali earth cuprates, $(Ca,Sr)_mCu_nO_z$). The secondary phases between Bi-2212 grains will greatly affect the texture alignments of plate like Bi-2212 grains. Meanwhile, the secondary phase precipitation will also change the chemical stoichiometry of Bi-2212 phase, thus leading to the degradation of superconducting properties[20-23]. Therefore, it is very important to control the phase evolution process during the partial melting process of Bi-2212 in order to obtain the Bi-2212 superconductors with optimized properties.

Based on the study of Bi-2212 phase diagram, the change of chemical stoichiometry in precursor powders has great effect on the phase evolution process [24,25]. Thus in our study, Bi-2212 precursor powders with different Cu ratios of x=2.0, 2.1, 2.2, 2.4 were synthesized to study the effect of Cu ratios on the phase composition and superconducting properties of Bi-2212 superconductors. Thick films with Ag substrate and

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Ag sheathed single filament tapes were fabricated by dip-coating process and powder in tube process, respectively. Critical current density was measured by a transport method at 77 K. The results from this paper can provide important information for the optimization of Bi-2212 superconducting wires for practical applications.

1 Experiment

$Bi_{2.1}Sr_{1.96}CaCu_xO_{8+\delta}$ (x=2.0, 2.1, 2.2, 2.4) precursor powders were prepared by a modified co-precipitation process[26] with the starting materials of Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO (> 99.9%) with the cation ratio of Bi:Sr:Ca:Cu = 2.1:1.96:1.0:x. Then a series of calcination processes in air at 740 °C/ 12 h, 800 °C/ 20 h, and 850 °C/ 20 h with intermediate grinding were performed to obtain the precursor powders with high Bi-2212 phase content. Bi-2212 thick films were fabricated by a dip-coating process. The paste for coating was made by mixing the precursor powders, the organic binder (polyvinyl butyral) and solvent (ethanol) with the mass ratio of 10:0.1:9. Meanwhile, Ag substrates with the dimension of 4 mm×20 mm×0.2 mm were cleaned by ultrasonic with ethanol and acetone. By dipping the substrate into the paste and lifting up with constant speed of 2 cm/s with self-made lifting device, the green films were obtained. Then these films were sintered at 150 °C for 2 h to get rid of the organics. Powder-in-tube process was adopted for the fabrication of Ag sheathed single filament tapes, by packing the precursor powders into Ag tubes, and a series of drawing and rolling process step by step. The cross section dimension of these single filament tapes is ~300 μm thick and ~4 mm wide. Partial melting process was applied on both thick films and tapes with the length of 5~10 cm. The partial melting processes of the films and tapes with different Cu ratios were optimized. Due to the different Ag ratio and oxygen partial pressure at the superconducting core, the optimized maximum heat treatment temperatures for thick films and tapes are 885 and 893 °C, respectively.

Polycrystalline X-ray diffraction (XRD) patterns on both powders and tapes were taken on an X-ray diffraction (XRD, Philips PW 1710) with Cu Kα radiation. The chemical compositions of precursor powders were measured by inductive coupled plasma atomic emission spectrometry (ICP-AES) with IRIS® Advantage ICP-AES and analyzed by normalizing the other cation contents to Bi ratio = 2.10. The back scattering morphology was observed by field-emission scanning electron microscopy (FESEM, JSM-6700F). The critical current, I_c, was measured at liquid nitrogen temperature (77 K) on a computer-aided apparatus using a DC four-probe method with the criterion of 1 μV/cm.

2 Results and Discussion

The chemical composition of Bi-2212 ($Bi_{2.1}Sr_{1.96}CaCu_x$-$O_{8+\delta}$) precursor powders were analyzed with ICP and the results are listed in Table 1. The increasing of Cu ratio is consistent with designed composition. The related physical properties are also listed in Table 1.

The precursor powders with different Cu ratios were sintered at 740, 800, and 850 °C step by step. The X-ray diffraction was performed after each step, with the patterns shown in Fig.1a~1c. After the sintering at 740 °C, the Bi-2201 phase appears to be the major phase with only small peaks represented for the newly formed Bi-2212 phase. It implies that higher temperature is necessary for the synthesis of Bi-2212 phase. Then after the sintering at 800 °C, the phase content of Bi-2212 increases greatly. Meanwhile, it is interesting to notice that the contents of residual Bi-2201 phase varies a lot with different Cu contents, which suggests that the phase evolution process changes with the variation of Cu ratio, due to the change of thermodynamic properties of involved phases. At last, with the sintering process at 850 °C, Bi-2212 phase becomes the major phase, with only small percentage of Bi-2201 and AEC phase (mainly the 1:1 AEC phase) residual. And the content of residual Bi-2201 phase decreases with increasing Cu ratio, while the content of AEC phase increases. Both suggest that the change of Cu ratio could influence the phase equilibrium during sintering.

The Bi-2212 phase content can be estimated with the following equation:

$$C_{2212} = \frac{\sum I_{2212}}{\sum I_{2212} + \sum I_{2201} + \sum I_{\mathrm{AEC}}} \times 100\% \quad (1)$$

where C_{2212} is the phase content of Bi-2212, I_{2212}, I_{2201}, and I_{AEC} represents the total diffraction intensity of Bi-2212 phase, Bi-2201 phase and AEC phase, respectively.

As shown in Fig.2, the phase evolution process obviously changes with different Cu ratios. With the same sintering temperature of 740 or 800 °C, the content of Bi-2212 phase increases with the increasing Cu ratio, which implies the

Table 1 Chemical composition of Bi-2212 ($Bi_{2.1}Sr_{1.96}CaCu_xO_{8+\delta}$) precursor powders and related physical properties

x	Chemical composition ratio				Bi-2212 content after 850 °C sintering/%	J_c /×1000 A·cm^{-2}	
	Bi	Sr	Ca	Cu		Thick film	Single filament tape
2.0	2.11 (8)	1.96	0.97 (0)	2.02 (8)	95.01	9.5	4.0
2.1	2.11 (9)	1.96	0.98 (4)	2.11 (0)	96.21	10.4	-
2.2	2.13 (4)	1.96	0.96 (9)	2.19 (9)	96.98	13.8	4.8
2.4	2.11 (7)	1.96	0.94 (9)	2.34 (6)	95.52	3.8	3.2