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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:

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

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

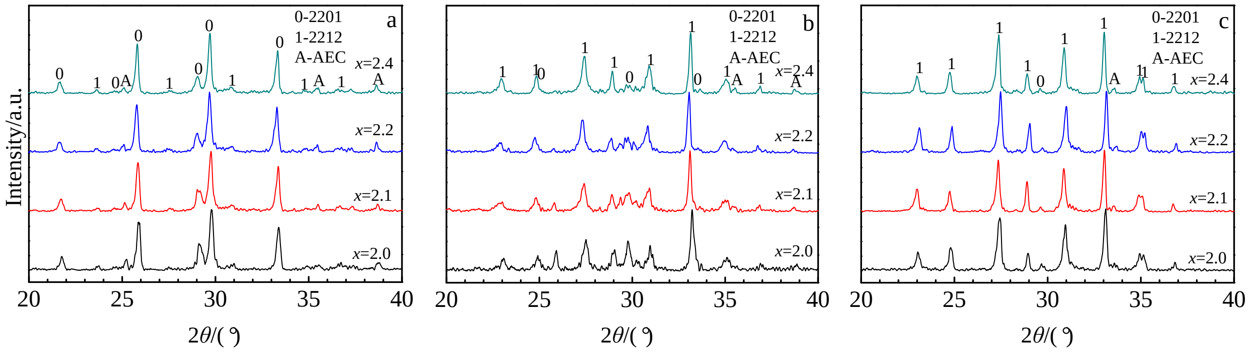

Fig.1 XRD patterns of precursor powders with different Cu ratios (x) after sintering at different temperatures: (a) 740 ^{o}C, (b) 800 ^{o}C, and (c) 850 ^{o}C

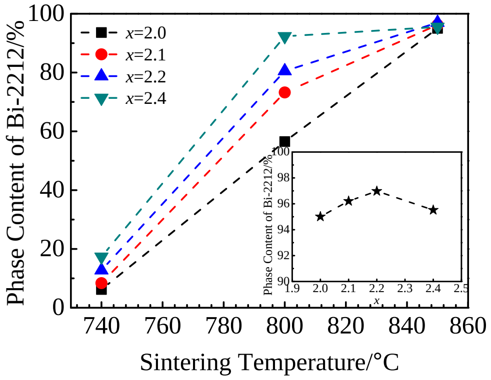

Fig.2 Phase content of Bi-2212 as a function of sintering temperature with different Cu ratios (the final phase content of Bi-2212 was plotted in the inset with the change of Cu ratio (x))

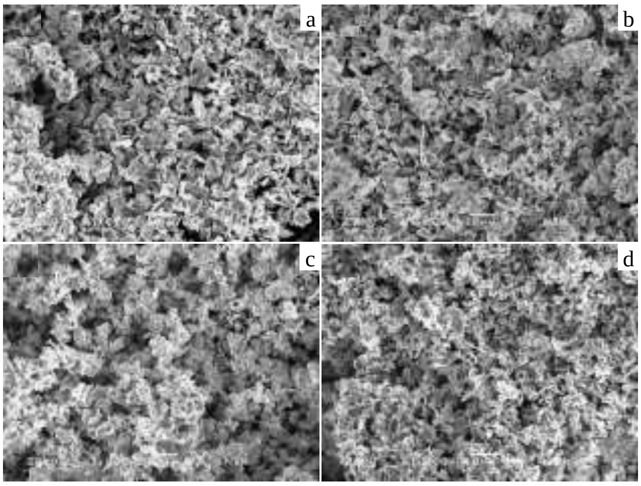

Fig.3 SEM images of precursor powders after 850 ^{o}C sintering with different Cu ratios: (a) x=2.0, (b) x=2.1, (c) x=2.2, and (d) x=2.4

decrease of formation temperature of Bi-2212 phase with increasing Cu ratio. Thus it is deduced that the change of phase evolution process can be attributed to the change of thermodynamic properties with Cu ratio. While after the sintering at 850 ^{o}C, which is very close to the peritectic temperature of Bi-2212 phase (~870 ^{o}C), Bi-2212 phase with a large Cu ratio already starts to decompose, thus leading to the decrease of the final Bi-2212 content. The maximum Bi-2212 phase content of ~97.0% is obtained with a proper Cu ratio of after the 850 ^{o}C sintering

SEM images of these precursor powders with different Cu ratios are shown in Fig.3. Plate-like particles with their surface parallel to the *ab* plane of Bi-2212 are obtained. All the powders exhibit the average grain size of ~50 μm, and no obvious difference can be noticed with different Cu ratios. This suggests that all the powders have gained their equilibrium state of crystallization and decomposition during the sintering process.

The Bi-2212 thick films are obtained with the dip coating technique combining with partial melting process using previously optimized heat treatment parameters. The X-ray diffraction patterns are obtained as shown in Fig.4, with the diffraction peaks of Bi-2212 phase indexed and marked on the plots. It can be obviously noticed that the Bi-2212 thick films with high oriented (00l) texture are obtained. Secondary phases, including Bi-2201 and AEC (mainly 14:24 AEC) are also observed. The content of secondary phase changes with different Cu ratio correspondingly, which can be explained with the influence of Cu ratio on the thermodynamic parameters of Bi-2212 as discussed above. The major secondary phase is Bi-2201. With the increase of Cu ratio to 2.1, the increasing Cu ratio is beneficial to the precipitation of AEC phase. Thus the contents of residual AEC phase and Bi-2201 phase both increase. With further increase of Cu ratio to 2.2, the increasing phase content of AEC and Bi-2201 changes the equilibrium state between crystallization and decomposition of Bi-2212 phase. Therefore, the phase content of Bi-2212 increases again, and the content of Bi-2201

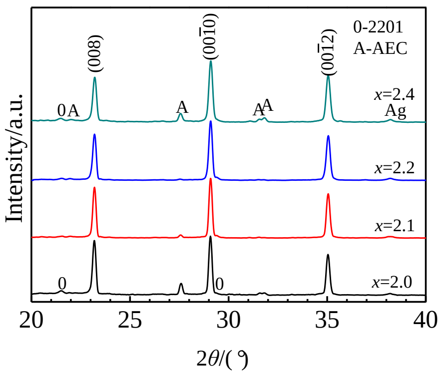

Fig.4 XRD patterns of thick films with different Cu ratios *x*, the diffraction peaks of Bi-2212 are index as marked on the plots (the Ag diffraction peak is from the Ag substrate)

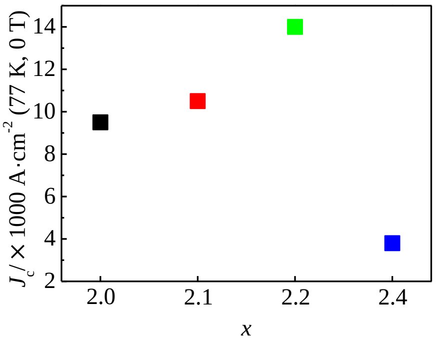

Fig.5 J_c of Bi-2212 thick films as the function of Cu ratio *x*

becomes the minimum. When the Cu ratio increased to 2.4, the AEC phase content increases again, due to the influence of Cu ratio as discussed above.

The critical current, I_c, of the thick films was measured at 77 K, self field. And the critical current density, J_c, was calculated as $J_c=I_c/A$, where *A* is the cross section of thick films, which is calculated based on the SEM images. It can be observed from Fig.5 that the critical current density increases gradually with the increasing Cu ratio from 2.0 to 2.2. Then it decreases severely when the Cu ratio increases to 2.4. The maximum J_c of 1.38×10^4 A/cm^2 is achieved with the $x=2.2$ film. This change of critical current density is mostly consistent with the change of phase content in the thick films. The major secondary phase in $x=2.0$ film is Bi-2201, while the major secondary phase in $x=2.1$ ~ 2.4 films becomes the AEC phase. The Bi-2201 grains mainly exist along the grain boundaries of Bi-2212 grains, which can severely affect the overall transport of current, and decrease J_c. Meanwhile, with the increase of Cu ratio, the stoichiometry of Bi-2212 phase also changes correspondingly, which leads to the optimal carrier concentration of superconducting phase, and thus larger critical current density.

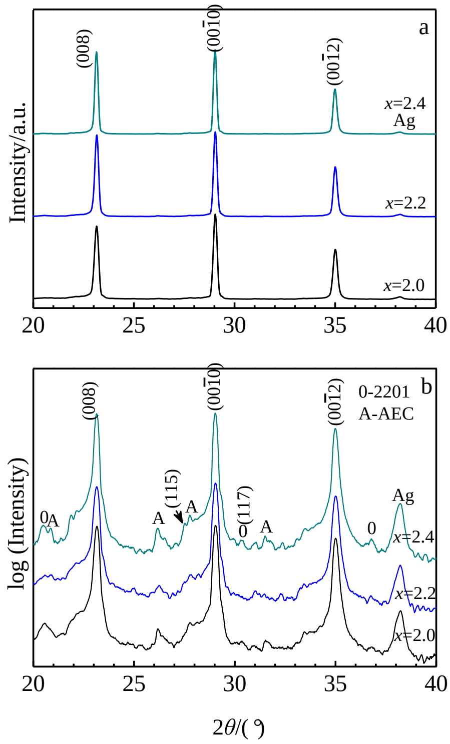

Fig.6 XRD patterns of Bi-2212 tapes with different Cu ratios of 2.0, 2.2 and 2.4

In order to further prove the effectiveness of Cu nonstoichiometry on the superconducting properties of Bi-2212 superconductors, Bi-2212 single filament tapes with Ag sheath were fabricated with the precursor powders of $x=2.0$, 2.2, 2.4 synthesized above. After the optimized partial melting process, the Ag sheath are pealed off and the X-ray diffraction patterns are obtained as shown in Fig.6. Highly (00*l*) textured structures are obtained in all these tapes. In Fig.6b, the XRD patterns are plotted with logarithmic coordinates, in which the diffraction patterns of secondary phases including Bi-2201 and AEC can be clearly observed. The change of secondary phase content is consistent with that in the thick films. The secondary phase content becomes the minimum with the Cu ratio of 2.2, and the content of AEC phase increases obviously with further increase of Cu ratio to 2.4.

Critical current values of these single filament tapes are measured with the same method as described above. The *V-I* curves of different tapes are shown in Fig.7a. The critical current increases with increasing Cu ratio from 2.0 to 2.2, and then decreases greatly due to the severe precipitation of secondary phase in $x=2.4$ tape. The critical current density values are also calculated and plotted in Fig.7b against the critical current density of thick films. It can be noticed that because the phase evolution processes are similar in both tapes and films, the changes of critical current density with Cu ratio are consistent with each other. The proper change of Cu ratio can optimize the phase evolution process of Bi-2212, therefore

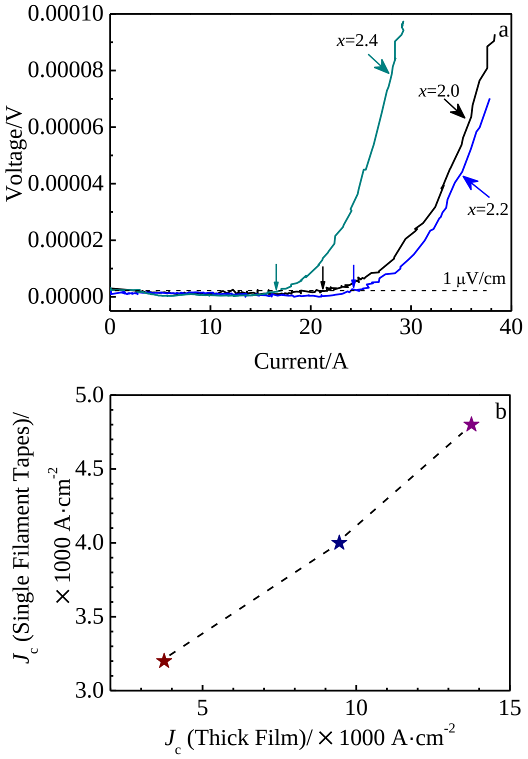

Fig.7 *I-V* curves of Bi-2212 thick films with different Cu ratios (a); the single filament tapes critical current density vs. the critical current density of thick films (b)

leading to the enhancement of transport properties. Besides, it should be noticed that the critical current density of thick films is larger than that of the tapes. Because the Ag layer has very important effect on the texture alignment of Bi-2212 grains during sintering, the Bi-2212 grains near the Ag substrates or Ag sheath have better alignment. The smaller thickness of superconducting layer in thick films can cause a larger ratio of high-texture areas, which increases the effective cross section during current transport and also increase transport properties. So by fabrication of multi- filamentary tapes of Bi-2212, the critical current density can be further improved. Meanwhile, the films are sintered in an open atmosphere, which is beneficial for the sufficient decomposition and recrystallization of Bi-2212 phase, which may be another possible reason for the larger current capacity of films than that of tapes.

3 Conclusions

1) Bi-2212 precursor powders with different Cu ratios are synthesized with modified co-precipitation process.

2) With the increase of Cu ratio, the formation rate of Bi-2212 phase increases monotonically during the 800 $^{\circ}$C sintering process.

3) The thick films and tapes are prepared by dip-coating and powder in tube process, respectively. The Cu ratio can also tune the secondary phase contents in both films and tapes consistently, therefore leading to the optimization of transport properties. The maximum critical current density of 1.38×10^4 A/cm^2 is obtained with the Cu ratio of 2.2 in thick films.

References

1 Gladyshevskii R, Musolino N, Flukiger R. *Phys Rev B*[J], 2004, 70: 184 522

2 Nicoletti D, Limaj O, Calvani P *et al*. *Phys Rev Lett*[J], 2010, 105: 077 002

3 Gomes K K, Pasupathy A N, Pushp A *et al*. *Nature*[J], 2007, 447: 569

4 Yang H B, Rameau J D, Johnson P D *et al*. *Nature*[J], 2008, 456: 77

5 Miao H, Marken K R, Meinesz M *et al*. *IEEE Trans Appl Supercond*[J], 2005, 15: 2554

6 Street A. *Spectroscopy Europe*[J], 2003, 15: 10

7 Godeke A, Cheng D, Dietderich D R *et al*. *IEEE Trans Appl Supercond*[J], 2007, 17: 1149

8 Weijer H W, Trociewitz U P, Marken *et al*. *Supercond Sci Technol*[J], 2004, 17: 636

9 Nakayama Y, Motohashi T, Otzschi K *et al*. *Phys Rev B*[J], 2000, 62: 1452

10 Vinu S, Sarun P M, Biju A *et al*. *Supercond Sci Technol*[J], 2008, 21: 045 001

11 Vinu S, Sarun P M, Shabna R *et al*. *Physica B*[J], 2010, 405: 4355

12 Christova K, Manov A, Nyhus J *et al*. *J Alloy Compd*[J], 2002, 340: 1

13 Bulaevskii L N, Daemen L L, Maley M P *et al*. *Physical Review B Condensed Matter*[J], 1993, 48: 13 798

14 Buhl D, Lang T, Gauckler L. *J Appl Supercond*[J], 1997, 4: 299

15 Stassen S, Vanderschueren A, Cloots R *et al*. *J Cryst Growth*[J], 1996, 166: 281

16 Jian J, Starch W L, Hannion M *et al*. *Supercond Sci Technol*[J], 2011, 24: 082 001

17 Jiang J Y, Miao H P, Huang Y B *et al*. *IEEE Trans Appl Supercond*[J], 2013, 23: 6 400 206

18 Eastell C J, Henry B M, Morgan C G *et al*. *IEEE Trans Appl Supercond*[J], 1997, 7: 2083

19 Tsay Y N, Li Q, Zhu Y *et al*. *IEEE Trans Appl Supercond*[J], 1999, 9: 1662

20 Majewski P. *Adv Mater*[J], 2004, 6: 460

21 Majewski P, Elschner S, Aldinger F. *Physica C*[J], 1995, 249: 234

22 Majewski P, Hettich B, Elschner S *et al*. *Appl Supercond*[J], 1994, 2: 93

23 Majewski P, Hettich B, Ruffer N *et al*. *Electronic Mater*[J], 1993, 22: 1259

24 Majewski P, Su H L, Hettich B. *Adv Mater*[J], 1992, 4: 508

25 Majewski P, Su H L, Quilitz M. *J Mater Sci*[J], 1997, 32: 5137

26 Mao C B, Du Z H, Zhou L. *Science in China*[J], 1996, E2: 181

Cu 含量变化对 **Bi-2212** 高温超导材料相演变过程及超导性能的影响

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摘　要：采用共沉淀工艺制备了不同 Cu 含量的 Bi-2212 前驱体粉末，并通过分步烧结工艺对前驱体粉末中不同 Cu 含量所引起的相演变过程的变化进行了系统分析。结合浸涂法和粉末装管法制备了 Bi-2212 厚膜及单芯线材。结果表明，Cu 含量的变化对厚膜和带材在烧结过程中的相演变过程同样具有极大的影响。随着 Cu 含量的增加，体系的相演化过程发生了改变。最终材料中 Bi-2201 相的含量逐渐减少，而 AEC 相的含量逐渐增加。考虑到 Bi-2201 和 AEC 对载流过程的影响各不相同，通过系统的优化，获得了最佳 Cu 含量为 $x=2.2$。在这一成分处，厚膜和单芯带材临界电流密度同时达到最大值。

关键词：高温超导材料；Bi-2212；非化学计量比；临界电流密度

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