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Effect of Ca Content on the Critical Current Density and Flux Pinning Properties of Ag sheathed Bi-2212 tapes

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Abstract

Single filament Ag sheathed Bi\textsubscript{2}Sr\textsubscript{1.98}Ca\textsubscript{x}Cu\textsubscript{2}O\textsubscript{8+δ} (Bi-2212) tapes with different Ca content of \(x=0.90, 0.95, 1.00,\) and 1.05, were prepared by powder in tube (PIT) process. The critical current density and flux pinning properties have been systematically studied with the variation of Ca content. X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been performed for the characterization of the tapes. Although the maximum critical current density, \(J_c\), was obtained from the stoichiometric sample under zero field, the nonstoichiometric Ca content are beneficial for the improvement of \(J_c\) under magnetic field, due to the enhancement of flux pinning. The \(J_c\) value of 950 A/cm\(^2\) has been obtained at 0.15 T, which is over 30% higher than that from \(x=1.00\) tape.

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1. Introduction

Bi-based superconductors are of great importance for the practical application as the high temperature superconductors (HTS). Bi\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{8} (Bi-2212), as the only materials so far, which can be made into isotropic round wires, has attracted more and more attentions [1-3]. Especially, due to the limitation of low-temperature superconductor Nb\textsubscript{3}Sn magnet, Bi-2212 insert coils have been considered to be a necessary part for manufacturing the high field (~30 T) magnet [4-7]. However, due to its intrinsic lattice structure, Bi-2212 exhibits strong anisotropic property, extremely short coherence length and large penetration depth [8], which lead to the rapid decrease of critical current density, \(J_c\), with applied magnetic field (\(J_c\)-\(B\) properties). Thus, for practical applications, it is very important to enhance its flux pinning properties.

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Among all the previous efforts made for the enhancement of the $J_c$-$B$ properties of Bi-2212 system, there are mainly two methods for the introduction of flux pinning centers. One is the directly embedded of nanosized particles. For example, the magnetization hysteresis has been significantly enhanced due to the introduction of nanosized MgO into Bi-2212/Ag tapes fabricated by dip-coating process [9]. The other way is by the substitution of Bi, Ca or Sr site. The substitution of Bi by Pb can obviously shorten the c-axis of Bi-2212 lattice, which both weakened the anisotropy of $J_c$ and enhanced the $J_c$-$B$ properties. And the substitution of Sr by rare earth (RE) elements, such as Ho, Eu, and Lu, can all improve the flux pinning properties of Bi-2212 [10-12]. We noticed that based on the layered structure of Bi-2212, Ca layer is located between two [Cu-O2] layers. Therefore, it is easier to tune the superconducting properties of Bi-2212 by doping on the Ca layer. In our study, four Bi-2212 single filament tapes with different Ca content varied from 0.90, 0.95, 1.00 to 1.05 were prepared in order to study the effect of Ca layer on the transport properties and flux pinning effect.

Nowadays, most of the researches are focused on the optimization of bulk Bi-2212 samples, and the critical current density was measured by magnetization method. For the practical applications, the most important parameter is the transport critical current density under magnetic field for PIT tapes and wires. In this study, single filament tapes were prepared by the powder in tube (PIT) technique combining with the partial melting process, starting from the precursor powders synthesized by co-precipitation process [13]. The critical current density was measured by transport method with an additional electromagnet, applying the magnetic field from 0 to 0.15 T. The results from this paper can provide important information for the practical fabrication of Bi-2212 insert coils.

2. Experimental

$\text{Bi}_2\text{Sr}_{1.96}\text{Ca}_x\text{Cu}_{2.0}\text{O}_{8+\delta}$ precursor powders with the $x$ value of 0.90, 0.95, 1.00 and 1.05 were prepared by co-precipitation process [14] with the starting materials of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, and CuO (> 99.9%). After a series of calcination processes in air at 800 °C/ 12 h, 820 °C/ 20 h, and 850 °C/ 20 h with intermediate grinding, the precursor powders were densely packed into Ag tubes, respectively. With the drawing and rolling process step by step, single filament tapes with the thickness of ~300 μm, width of 4 mm were obtained.

During the partial melting process, the maximum heat treatment temperature, $T_{\text{max}}$, is the key parameter for the superconducting properties of the final tapes. $T_{\text{max}}$ of 891, 892, 893, and 894 °C have been used to decide the optimized heat treatment parameter. The tapes were heated to $T_{\text{max}}$, until the Bi-2212 were melted and kept at $T_{\text{max}}$ for 20 min, then cooled down with the cooling rate of 5 °C/h to the annealing temperature of 840 °C and kept at 840 °C for 20 h.

X-ray diffraction (XRD) patterns were taken on a X-ray diffraction (XRD, Rigaku D/MAX2000PC) with Cu-Kα radiation. The back scattering morphology was taken by field-emission scanning electron microscopy (FESEM, JSM-6700F). The compositional analysis was taken by Inca-X-Stream Energy-dispersive X-ray spectroscopy (EDX). The chemical compositions of precursor powders were measured by inductive coupled plasma atomic emission spectrometry (ICP-AES) with IRIS® Advantage ICP-AES. 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. The additional magnetic field was applied by a Bi-2212 magnet fabricated by our own lab. The magnetic field as a function of input current has been confirmed by Hall Effect sensor.

3. Results and Discussions
Bi-2212 precursor powders were obtained with different Ca content. As shown in Fig. 1 (a), the diffraction peaks can be indexed into an orthorhombic structure (A2aa) with the JCPDS Card No. 46-0431. Meanwhile, it can be noticed that the diffraction peak of all the samples shifted to the left first then to right at \( x = 1.05 \), which implied the increase of lattice parameters until \( x = 1.00 \) then decrease with further increase of Ca content. The increase of Ca content from 0.90 to the stoichiometric value (\( x = 1.00 \)) lead to the extension of lattice. And with the further increase of Ca content, additional oxygen has been incorporated into Bi-O layers to keep the charge neutrality, which caused the reduction of the net positive charge in the Bi-O layers. This finally appeared as the decrease of lattice parameter (especially c-axis length). The ICP-AES results of Ca content normalized to Bi content of 2.1 has been shown in Fig. 1 (b), which confirmed the chemical composition of these precursor powders.

Based on the previous experiences, Bi-2212 tapes are very sensitive to the maximum heat treatment temperature, \( T_{\text{max}} \). Therefore \( T_{\text{max}} \) has been tuned from 891 to 894 °C. After the sintering process, critical current, \( I_c \), was measured and critical current density, \( J_c \) was calculated by \( J_c = I_c / A \), where \( A \) is the cross section area measured through observation of optical microscope. As shown in Fig. 2, it can be obviously noticed that the optimized \( T_{\text{max}} \) value should be 893 °C for all the four samples. Thus the measurements of \( J_c-B \) properties were taken on the tapes sintered at 893 °C.

The X-ray diffraction patterns of the final tapes sintered at 893 °C are shown in Fig. 3. All the four tapes exhibited very strong (00l) textures, with the texture degree of (00l) over 97.5%. In order to show the details of the secondary phases, the intensity has been plotted in to logarithm in the inset. Besides the main phase Bi-2212, there are mainly two secondary phases in the final tapes, Bi\(_2\)Sr\(_2\)CuO\(_x\) (Bi-2201, JCPDS # 39-0283) and SrCaCu\(_2\)O\(_4\) (1:1 AEC, JCPDS # 48-0219). It can be observed that with the
increase of Ca content from 0.90 to 1.05, Bi-2201 phase slightly decreased while 1:1 AEC phase became more detectable.

![XRD patterns of Bi-2212 tapes with different Ca content. Details can be seen from the inset pattern with the intensity plotted in logarithm](image)

The morphology and phase distribution change due to the variation of Ca content were observed by cutting along the rolling direction and polishing the vertical sections, as shown in Fig. 4 (a~d). The thicknesses of the filament for the four tapes are 200, 184, 170, and 140 μm, respectively. The differences were caused during the rolling process. In the $x = 0.90$ tape, Bi-2201 stripes (colored in white), are distributed along the grain boundaries of Bi-2212. And only small particles of 1:1 AEC (in black) can be observed. With the increase of Ca content, the Bi-2201 content decreased accordingly, while both the particle size and the ratio of 1:1 AEC phase increased obviously. This result is consistent with the previous analysis by XRD patterns, suggesting that the Ca content can influence the phase transition process during the partial melting process. Meanwhile, in order to make sure the Ca content in the Bi-2212 phase is still different from $x = 0.90$ sample to $x = 1.05$ sample, the chemical compositions of Bi-2212 was taken by EDX as shown in Fig. 5. The inset in Fig. 5 (a) proved the increasing content of Ca in different samples.

![SEM pictures of Bi-2212 tapes (a) Ca=0.90, (b) Ca=0.95, (c) Ca=1.00, (d) Ca=1.05, after the heat treatment.](image)
The $J_c$ values of these four tapes under the magnetic field from 0 to 0.15 T were calculated and plotted as a function of magnetic field. As shown in Fig. 6 (a), the critical current density $J_c$ of different tapes was plotted. The maximum $J_c$ was obtained from the tape with Ca content of $x=1.00$. This implied that the stoichiometric sample was already in “optimally-doped” area after the partial melting process, while the increase and decrease of hole carriers by decrease and increase of Ca content can shift the superconducting phase into the “over-doped” and “under-doped” state, respectively. However, with the increasing magnetic field, the $J_c$ values of $x=1.00$ tape decreased rapidly. At the magnetic field of $B=0.15$ T, the $J_c$ values increased with the increasing Ca content. The optimized $J_c$ value of 950 A/cm$^2$ was obtained at $x=1.05$, which is over 30% higher than $J_c$ of $x=1.00$. Therefore, the Bi-2212 tape with the Ca content of $x=1.05$ shows more advantages for the application under magnetic field.

The normalized critical current density $J_c/J_0$ under magnetic field, where $J_0$ is the critical current density value at zero field, was shown in Fig. 6 (b), which can imply the flux pinning properties. Although the maximum $J_c$ was obtained at $x=1.00$ sample, all the $J_c/J_0$ values of nonstoichiometric samples are higher than that from $x=1.00$ tape, which indicated the enhancement of transport properties under magnetic field. Considering with the smaller lattice parameters obtained from XRD patterns, it can be concluded that the nonstoichiometric Ca content can enhance the flux pinning in Bi-2212 systems. Because in Bi-2212 systems, the flux lines undergo a crossover from 3D flux lines to 2D pancake vortices at higher fields and temperatures. The 2D pancake vortices are mainly confined in the [Cu-O2] layers. The crystal defects created by Ca nonstoichiometry are much closer to the two [Cu-O2] layers, which can effectively pinned the strongly coupled vortices and lead to the enhancement of flux pinning properties in Bi-2212.

**Fig. 6 (a) Plots of critical current density values vs magnetic field. (b) Normalized critical current density $J_c/J_0$ of Bi-2212 tapes with different Ca content as a function of Magnetic field from 0 to 0.15 T.**

### 4. Conclusion

The critical current density and flux pinning properties of single filament Ag sheathed Bi$_{2.1}$Sr$_{1.96}$Ca$_x$Cu$_{2.0}$O$_{8+8}$ tapes with different Ca content have been systematically investigated. The Ca content can influence the phase composition after the partial melting process, thus different secondary phase distribution can be observed in the tapes with different Ca content. Although at zero field, the maximum $J_c$ value was obtained on $x=1.00$ tape, the $J_c$-$B$ properties of nonstoichiometric samples have been greatly enhanced, contributed to the crystal defects introduced by the variation of Ca content. Under the magnetic field of 0.15 T, the $J_c$ values of $x=1.05$ tape has been improved for over 30% comparing
with the $J_c$ of $x=1.00$ tape. Therefore, for the practical applications of Bi-2212 as the insert coils, the variation of Ca content can be an easy and effective way to improve the $J_c$-$B$ properties.

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