

Influences of Na Doping on Superconducting Properties of Bi-2212 High Temperature Superconductors

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Abstract: Polycrystalline bulks $\text{Bi}_{2.1}\text{Sr}_{1.96}\text{Ca}_{1-x}\text{Na}_x\text{Cu}_{2.0}\text{O}_{8+\delta}$ (Bi-2212) with Na doping content of $x=0, 0.02, 0.05, 0.10$ (at%) were fabricated by spark plasma sintering (SPS) process. The Bi-2212 precursor powders were synthesized by modified co-precipitation process, and NaOH powders were added as dopants before calcination. The influences of Na^+ ion doping on lattice parameters, phase composition, microstructures as well as related superconducting properties were investigated. The results show that introduction of Na in Bi-2212 system can cause an obvious decrease in phase transition temperatures. Thus during the SPS process, although the sintering temperature is greatly decreased, Na doped Bi-2212 bulks still tend to decompose into $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Bi-2201) phase, which leads to the decrease of both superconducting phase content and texture degrees, thus causing negative effects on superconducting properties. In addition, Na doping introduces more point defects into Bi-2212 matrix, which act as flux pinning centers during current transport process, and contribute to the increase in current capacity under high field. Therefore, Na doping with optimized sintering parameters should be considered as a promising method to enhance the high field current capacity of Bi-2212 system.

Key words: high temperature superconductor; chemical doping; flux pinning mechanism; critical current density

Since the first discovery of Bi-based superconductors, including $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Bi-2223), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212) and $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Bi-2201), with the critical temperature T_c of 110, 80, and 30 K, respectively, they have attracted much attention due to their different but excellent superconducting properties. Bi-2212 based superconductors have been considered as one of the most promising practical high-temperature superconductors (HTS) under low-temperature and high magnetic field, due to their excellent properties, including the high irreversibility field H_{ir} , beyond $100 \text{ T}^{[1]}$ and the large critical current density J_c , exceeding $266 \text{ A}\cdot\text{mm}^{-2}$ up to $45 \text{ T}^{[2]}$. Besides, as the only HTS so far, Bi-2212 can be made into round wires with isotropic cross sections, which can greatly simplify the winding process for cables and magnets. Therefore, they have attracted much attention for their practical applications as insert coils in high field magnets and Rutherford cables for accelerators^[3-9].

However, there are two factors which still restrict the transport properties of Bi-2212 superconductors. One is the weak intergranular links due to the low texture degree^[10-13], high porosity^[14, 15] and/or grain boundaries with secondary phases or amorphous layers^[16, 17]. The other is the weak flux pinning property in the direction perpendicular to ab plane, which can be attributed to its intrinsic pancake lattice structure^[18]. Therefore, optimization processes are required aiming at obtaining Bi-2212 superconductors with high superconducting phase content, highly orientated grains, denser structures, clean grain boundaries and strong flux pinning property to improve the current carrying capacity of Bi-2212 wires. Based on previous studies, chemical doping can introduce different influences on the phase transition process, lattice parameters, as well as superconducting properties. The doping of Pb at Bi site in Bi-2212 matrix has

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been considered to be the most successful method^[19-22]. The introduction of Pb^{2+} ions enhances the attraction between Bi-O layers, thus decreasing the lattice parameter c of Bi-2212, which obviously reduces the anisotropic behavior of superconducting properties and also introduces effective flux pinning centers to enhance the current capacity under high field. The doping of rare earth (RE) elements at the Sr or Ca site of Bi-2212 has also been systematically studied^[23-32]. And in many reports, the introduction of RE ions including Gd^{3+} , Ho^{3+} , Yb^{3+} and Eu^{3+} can enhance the flux pinning properties by forming effective pinning centers in the BSCCO system. In addition, chemical doping can also lead to the change of microstructure by tuning their thermodynamic properties of Bi-2212. B_2O_3 doping results in the faster growth and better alignment of the Bi-2223 grains, which also improve the critical current density. And even secondary phase addition such as Al_2O_3 , CaZrO_3 , and ZrO_2 can be useful to improve the overall performance of Bi-2212 by alleviating the constraints of the melt processing step^[33,34]. Therefore, it is interesting and necessary to study the doping effects of other elements on Bi-2212 to further improve its superconducting properties.

In this study, Na was chosen as the dopant to be incorporated into the Bi-2212 matrix by mixing NaOH with Bi-2212 precursors before calcination. It was found that Na doping can greatly influence the thermodynamic parameters of Bi-2212 system. Therefore, during the spark plasma sintering process, the sintering temperature was optimized accordingly based on a large number of experiments to achieve the optimal sintering bulks. The change of lattice parameters proved the entering of Na^+ ions into Bi-2212 matrix, and the change of Na doping site from Bi-2212 matrix to Bi-2201 matrix was also noticed based on X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Then, the influences of Na doping on the microstructures as well as superconducting properties, including critical temperature T_c , and critical current density J_c were also systematically studied.

1 Experiment

$\text{Bi}_{2.1}\text{Sr}_{1.96}\text{Ca}_{1-x}\text{Cu}_{2.0}\text{O}_{8+\delta}$ ($x=0, 0.02, 0.05, 0.10$, at%) precursor powders were firstly prepared by modified co-precipitation process^[24] with the raw materials of Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO (>99.9%). NaOH was then weighed as the atomic ratio corresponding to the x value and mixed with obtained Bi-2212 precursors before the calcination process. Na doped Bi-2212 precursor powders were obtained 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. Silver crucibles were adopted for the calcination in order to avoid the contamination of powders. The precursor powders were then densely packed into a graphite die and sintered into pellets with the diameter of ϕ 12.7 mm and thickness of ~1.5 mm by spark plasma sintering technique, with proper sintering temperature, and sintering time of 5 min under the uniaxial

pressure of 60 MPa.

The thermodynamic properties of Bi-2212 precursor powders with and without NaOH doping were analyzed by differential scanning calorimetry (DSC, NETZSCH STA409PC) in ambient atmosphere with the heating rate of 10 °C/min. Polycrystalline X-ray diffraction patterns of bulks were obtained by X-ray diffractor (XRD, Bruker D8 Advance) with $\text{Cu-K}\alpha$ radiation ($\lambda=0.1542$ nm). The texture degrees along c -axis orientation were mostly used to assess the quality of textural structures, which were calculated as:

$$F_{00l} = \frac{\sum I_{00l}}{\sum I} \times 100\% \quad (1)$$

where I_{00l} represents to the intensity of (00 l) diffraction peaks of Bi-2212, $\sum I$ is the total diffraction intensity of the pattern. The density of bulks was measured using the standard Archimedes method. The fracture surface was observed by scanning electron microscopy (SEM, JEOL JSM-6700F). The compositional analysis was performed by Inca-X-Stream energy-dispersive X-ray spectroscopy (EDX) to recognize the phase distribution. X-ray photoelectron spectroscopy observation (ESCALAB 250Xi Thermo SCIENTIFIC, $\text{Al K}\alpha$ radiation) was performed on Bi-2212 bulks. The surface of bulks was carefully cleaned and swept with argon gas for 5 min before XPS. The total acquisition time was 3 min with the binding energy ranging from 0 eV to 1350 eV and the energy step was 0.05 eV. The temperature dependence of magnetization from 4.2 K to 120 K and magnetic hysteresis loops under 4.2 K from 0 T to 6 T of the specimens cut from the obtained SPS pellets with the dimension of ~2 mm×2 mm×1.5 mm were measured by the superconducting quantum interference device (SQUID). The 2 mm×2 mm surface was parallel to the pellet plane. During the measurements, specimen was put into a capsule with its 2 mm×2 mm surface perpendicular to the magnetic field direction and it was fixed with low-temperature glue to avoid any movements of specimen in magnetic field or during cooling. Bean model^[35] was adopted to calculate the critical current density (J_c) as follows:

$$J_c = \frac{20\Delta M}{b(1-b/3a)} \quad (b < a) \quad (2)$$

where a and b are the length and width of the specimen, respectively, which are both perpendicular to the applied magnetic field, and ΔM is the difference between M^* and M under the same magnetic field.

2 Results and Discussion

In order to examine the effects of Na doping on the thermodynamic properties of Bi-2212 system, DSC curves of pure Bi-2212 powders and Na doped Bi-2212 powders with $x=0.10$ are both obtained and plotted in Fig.1. It can be observed that during the heating process, only one peak appears at ~850 °C on each curve, which represents the melting and decomposition of Bi-2212 phase. Differential

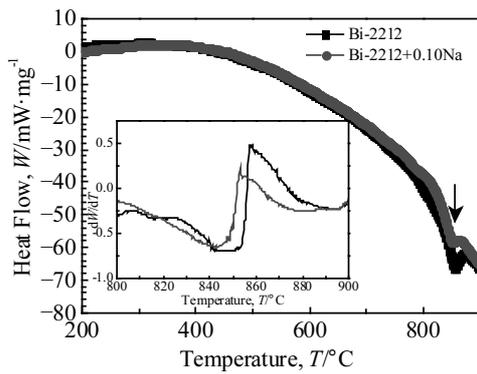


Fig.1 DSC curves of pure Bi-2212 powders and Na doped Bi-2212 powders with $x=0.10$ (inset is differential plots of two curves)

curves are obtained and plotted in the inset, in order to show the difference more clearly. The melting temperature difference of ~ 4.7 K can be attributed to the introduction of Na, which suggests that Na doping can obviously influence the thermodynamic parameters of Bi-2212 system. Thus during the SPS process, different sintering temperatures of 830, 800, 770, and 660 °C were adopted for the sintering of Na doped Bi-2212 with $x=0, 0.02, 0.05, 0.10$. The change of sintering temperature is much more significant than that of melting point acquired from DSC plots, because during the SPS process, the real temperature inside the samples is higher than the nominal value. Therefore, in order to avoid severe melting of the samples during SPS process, much lower temperatures should be adopted. And all these sintering temperature values were obtained based on a large number of experiments.

After the SPS process at different sintering temperatures, Bi-2212 bulks with different Na doping contents are obtained. The density of these bulks was measured. As listed in Table 1, after the optimized sintering process based on different chemical compositions, the density of these bulks is different. The density values increase from 6.07 g/cm^3 to 6.30 g/cm^3 at the Na doping content of 0.02 at%, and then decrease to 6.16 and 6.08 g/cm^3 with further increasing the Na content. Generally speaking, the decrease of sintering temperature always leads to the decrease of bulk density. However, with changing the sintering temperature from 830 °C to 800 °C for pure Bi-2212 and Bi-2212 with 0.02 at% Na, the bulk density increases obviously. This phenomenon can be explained by the change of thermodynamic parameters caused by Na doping. In addition, the decrease of density with further introduction of Na can be attributed to both the change of sintering behavior, which can influence the orientation growth process of Bi-2212 grains, and different phase compositions, which will be discussed later.

The X-ray diffraction patterns of bulks after SPS are plotted in Fig.2. Bi-2212 is the major phase in all these bulks. However, when the Na doping content is larger than 0.05 at% ($x \geq 0.05$),

Table 1 Microstructural and physical parameters of Na doped Bi-2212^[9]

Parameter	$x=0$	$x=0.02$	$x=0.05$	$x=0.10$
Peak position of (008) for Bi-2212 phase	23.069	23.064	23.072	23.072
Peak position of (0010) for Bi-2212 phase	28.939	28.920	28.928	28.927
Peak position of (0012) for Bi-2212 phase	34.900	34.872	34.877	34.893
Peak position of (006) for Bi-2201 phase	-	-	21.861	21.764
Peak position of (008) for Bi-2201 phase	-	-	29.193	29.164
Melting point/°C	857.6	-	-	852.9
Density/g·cm ⁻³	6.07	6.30	6.16	6.08
Bi-2212 content/%	98.8	98.0	83.2	82.1
Texture degree/%	57.9	68.8	59.6	49.6
FWHM of (0010)/(°)	0.129	0.132	0.147	0.162
XPS peak area of Na/cps	-	2721	5724	7005
Average grain radius/μm	4.3(2)	4.1(8)	2.8(8)	2.2(2)
Critical temperature, T_c /K	85	82	81	79
$\Delta M @ 4.2 \text{ K}$ on ZFC curves/ $\text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$	0.195	0.185	0.178	0.167

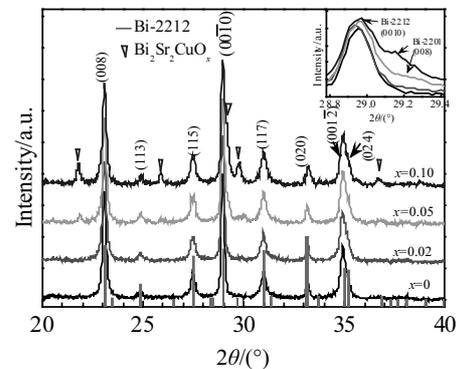


Fig.2 XRD patterns of SPS sintered Bi-2212 bulks with different Na contents

obvious Bi-2201 diffraction peaks can be observed, as marked by triangles. In addition, (00 l) texture is obtained in these bulks. The (00 l) texture degree values are obtained by Eq.(1) and listed in Table 1. With the increase of Na content to $x=0.02$, the texture degree of obtained bulks increases firstly from 57.9% to 68.8%, and then decreases to 49.6% with further increasing Na content to $x=0.10$. The Full-width at half maximum (FWHM) value is also estimated based on the XRD pattern, as listed in Table 1. The increase of FWHM value is negligible at the Na content of $x=0.02$. While with further increase of Na content, the FWHM values increase obviously from $\sim 0.132^\circ$ to 0.162° . Based on the analyses of Scherrer equation, this increase of FWHM corresponds to the decrease of average particle size of Bi-2212 by nearly 20%. According to the above results, the formation of (00 l) textures with the texture degree larger than 50% implies that the SPS process can also be recognized as a partial melting process for Bi-2212. During the sintering of pure Bi-2212 and 0.02 at% Na-doped Bi-2212 bulks, texture Bi-2212 grains can be obtained with undetectable content of secondary phase. However, due

to the dramatic change of thermodynamic parameters with high content of Na doping, more Bi-2212 phases decompose and form Bi-2201 phases, which also affect the orientation growth of Bi-2212 lamellar grains. Therefore, when the Na doping content is higher than 0.05 at%, the obtained Bi-2212 bulks exhibit smaller grains, less textural structures and more secondary phases, which will all influence the superconducting properties of Bi-2212.

Another effect of Na doping is the change of lattice parameters. As shown in the inset in Fig.2, under different Na doping contents, the diffraction peak positions of both Bi-2212 and Bi-2201 phase change correspondingly. With the introduction of 0.02 at% Na, the diffraction peaks shift towards lower degrees, which suggests the increase of lattice parameters. However, the change of lattice parameter is not monotonic. The further increase of Na content to $x=0.05$ causes the peak to shift towards higher degrees, which implies the decrease of lattice parameters. When Na content is 0.10 at%, the peaks are almost at the same position with those of $x=0.05$ bulk. Meanwhile, the shift of Bi-2201 peaks towards lower degrees can be observed, as marked by arrows and listed in Table 1. It is interesting to deduce that with small Na content, there is almost no Bi-2201 phase. All the Na^+ ions enter into Bi-2212 matrix, which causes the increase of lattice parameter c due to the weakening of attractive force between layers with Na^+ substitution at Ca^{2+} site. However, when Bi-2201 phase appears, most of the Na^+ ions tend to enter into

Bi-2201 matrix instead of Bi-2212 due to smaller activation energy of incorporation, which contributes to the obvious change of Bi-2201 lattice structure rather than Bi-2212. This dynamic process of doping can also influence the superconducting properties of obtained Bi-2212 bulks, and it will be further confirmed by XPS in the follows.

XPS spectra of all the samples are obtained and the characterization peaks of Na element are fitted and analyzed, as shown in Fig.3. According to Fig.3a, it can be clearly observed that the characterization peak of Na only exists in the Na doped samples. The peak area increases with increasing the Na content consistently, as listed in Table 1. However, the shift of Na peaks is quite obvious, which suggests that there are two different chemical environments for Na^+ ions. By fitting these patterns, as shown in Fig.3b~3d, the shift of peaks can be clearly observed. In the bulk with Na content of $x=0.02$, the peak appears at the binding energy of 1072.27 eV. While with the increase of Na content to $x=0.05$, two different peaks exist simultaneously at the binding energy of 1072.39 and 1071.09 eV. In the bulk with the largest Na content of $x=0.10$, only one Na peak appears at the binding energy of 1071.88 eV. Therefore, it can be deduced that Na^+ ions occupy two different lattice sites. When the doping content is small, there is only Bi-2212 phase. Na^+ ions enter into Bi-2212 matrix with the binding energy of 1072.27 eV. However, when the Bi-2201 phase first appears under Na content of 0.05 at%, Na^+ ions occupy the lattice sites in Bi-2212 and Bi-2201 at the same time. And when the Bi-2201 phase

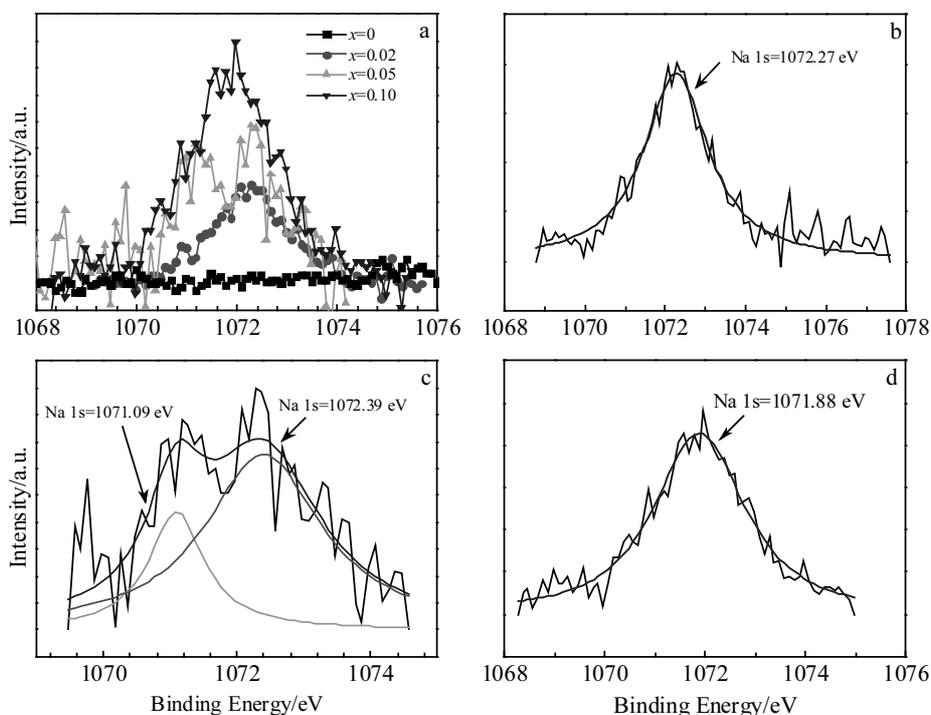


Fig.3 XPS spectra of Bi-2212 bulks with different Na doping contents (a); fitted profile of XPS spectra of Na-doped Bi-2212: (b) $x=0.02$, (c) $x=0.05$, and (d) $x=0.10$

content is large enough to receive all the Na⁺ ions, all the Na⁺ ions enter into Bi-2201 matrix with a smaller binding energy. This analysis is consistent with the analysis based on XRD. Therefore, the dynamic doping process of Na can be confirmed.

The microstructures evolution with Na doping content is analyzed by SEM. As shown in Fig.4, in all these images, textural structures with Bi-2212 lamella are clearly observed. As listed in Table 1, the average grain size decreases from 4.3 μm to 2.2 μm with increasing Na doping content from 0 to 0.10 at%. Meanwhile, under higher Na content of 0.05 at% and 0.10 at%, Bi-2201 particles appear at the grain boundary of Bi-2212 lamellar as marked by arrows in Fig.4d. Therefore, the decrease of grain size can be attributed to both the high

nucleation rate during sintering due to the change of thermodynamic parameters and the appearance of large contents of secondary phase which can block the growth of grains. Both the small particle size and existence of Bi-2201 at grain boundaries will act as intergrain weak links during current transport.

The temperature dependence of magnetization curves are measured and shown in Fig.5, in which the superconducting transition area is zoomed in the inset. It can be clearly observed that the maximum critical temperature T_c of 85 K is obtained in the pure sample. With the increase of Na doping content, T_c decreases monotonically to 82, 81 and 79 K. The decrease of T_c of pure sample and 0.02 at% Na doped sample should be attributed to the entering of Na⁺ ions into Bi-2212

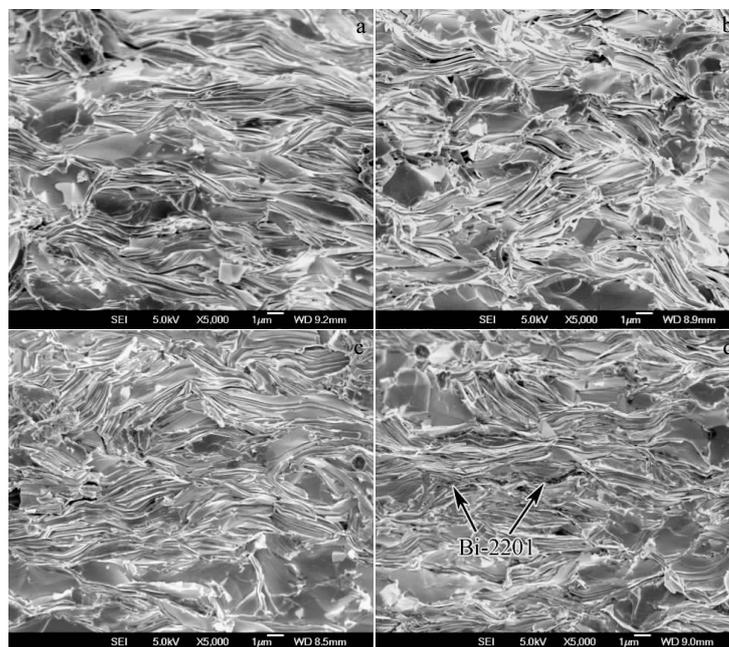


Fig.4 SEM images of fractural surface of Bi-2212 bulks with different Na contents: (a) $x=0$, (b) $x=0.02$, (c) $x=0.05$, and (d) $x=0.10$

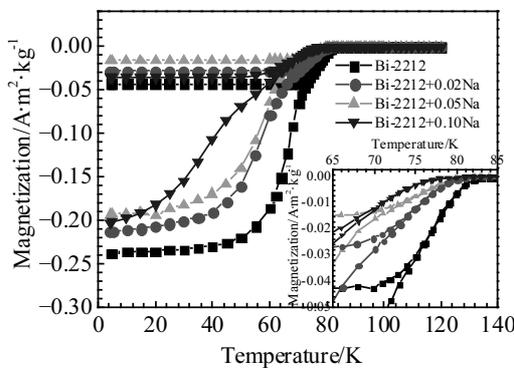


Fig.5 Temperature dependence of magnetization curves of Bi-2212 bulks with different Na contents (superconducting transition region is zoomed in the inset)

matrix, which changes the carrier concentration and influences the superconducting transition of Bi-2212. With higher Na doping content, the decrease of T_c can also be attributed to the appearance of Bi-2201 phase, which leads to the chemical composition variation of Bi-2212. The ΔM value at 4.2 K, which is always recognized as a measure of superconducting phase volume ratio, also decreases monotonically by nearly 14% from 0.195 to 0.167 $A \cdot m^2 \cdot kg^{-1}$. It can be explained by both the appearance of Bi-2201 phase and the chemical variation of Bi-2212 phase.

The hysteresis loops of all these samples were also obtained and the critical current density (J_c) was calculated using Bean model in Eq.(2). As shown in Fig.6a, the maximum J_c value is obtained for pure Bi-2212 bulks under self-field. With the increase of Na doping content, the self-field J_c value decreases. In addition, the decrease of J_c with magnetic field can also be

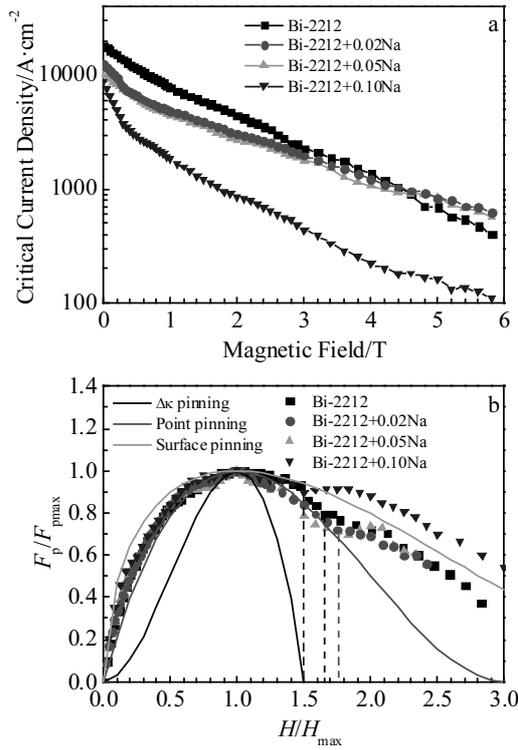


Fig.6 Critical current density calculated based on hysteresis loops using Bean model (a), and the magnetic field dependence of normalized flux pinning force (b) (turning points of $f^*(h^*)$ curves from point pinning to surface pinning are marked with dashed lines)

clearly observed. However, the decreased slopes are different from Na doping. Smaller decrease in slopes is obtained when Na doping content is 0.02 at% and 0.05 at%. Therefore, higher J_c is obtained under the magnetic field higher than 4.5 T.

In order to explain the change of decreased slopes of $J_c-\mu_0H$ curves with Na doping, flux pinning behaviors of all these samples are analyzed. Generally speaking, reduced pinning force density $f = F_p/F_{pmax}$ (F_p is the calculated pinning force density, $F_p = J_c \times \mu_0 H$; F_{pmax} is the maximum pinning force density value) often scales monotonically with reduced magnetic field $h = H/H_{irr}$ ($\mu_0 H_{irr}$ is the irreversibility field). But it is difficult to determine the $\mu_0 H_{irr}$ value accurately considering the high irreversibility field of Bi-2212. Therefore, in this study, aiming at minimizing the uncertainty in the pinning analysis, $F_p-\mu_0 H$ data are rescaled by $h^* = H/H_{max}$ (where $\mu_0 H_{max}$ is the magnetic field when F_p reaches the maximum value) as widely adopted. The scaling of $f^*(h^*)$ data can be given by the following equations:

$$\frac{1}{3} f^*(h^*) = h^{*2} \left(1 - \frac{2}{3} h^*\right) \quad (\Delta k \text{ pinning}) \quad (3)$$

$$\frac{4}{9} f^*(h^*) = h^* \left(1 - \frac{h^*}{3}\right)^2 \quad (\text{normal point pinning}) \quad (4)$$

$$\frac{16}{25} f^*(h^*) = h^{*1/2} \left(1 - \frac{h^*}{5}\right)^2 \quad (\text{surface pinning}) \quad (5)$$

As shown in Fig.6b, all the samples follow a mixed pinning mechanism of point pinning and surface pinning, between which point pinning is the major mechanism under low field. While with the increase of magnetic field, the major pinning mechanism changes to surface pinning. This is because the pinning strength of point pinning is too weak under high field. The turning point from point pinning to surface pinning can be used to measure the strength of point pinning centers. With the increase of Na doping, the turning point shifts from ~ 1.65 to 1.75, and then decreases to 1.5 as marked by the dashed lines. The slight enhancement of point pinning strength under Na doping content of 0.02 at% and 0.05 at% can be attributed to the introduction of Na^+ ions into Bi-2212 matrix, which leads to the formation of more point pinning centers.

3 Conclusions

1) Due to the change of thermodynamic parameters with Na doping, the sintering temperature decreases from 830 °C to 660 °C, while a large number of Bi-2201 phases still appear after sintering due to the decomposition of Bi-2212.

2) The occupancy of Na^+ ions changes from Bi-2212 matrix to Bi-2201 matrix due to the smaller binding energy.

3) Na doping is harmful to the critical temperature of Bi-2212, which also decreases the superconducting phase volume ratio. However, with proper amount of Na doping, high field current capacity is improved due to the formation of more effective point pinning centers, which may be beneficial to the optimization of Bi-2212 wires for high field applications.

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Na 掺杂对 Bi-2212 高温超导体性能的影响

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摘要: 采用放电等离子烧结 (SPS) 工艺制备了 Na 掺杂的 $\text{Bi}_{2.1}\text{Sr}_{1.96}\text{Ca}_{1-x}\text{Na}_x\text{Cu}_{2.0}\text{O}_{8+\delta}$ 超导材料。Bi-2212 前驱体粉末采用改进的共沉淀工艺制备, 并在烧结前将前驱体粉末与 NaOH 混合。研究了 Na 离子掺杂对 Bi-2212 体系晶格结构、相组成、微结构和相关超导性能的影响。结果表明: Na 离子掺杂导致 Bi-2212 体系相转变温度的显著降低, 因此在 SPS 过程中, 烧结温度相应发生了变化。但 Na 掺杂仍然导致大量 $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Bi-2201) 相生成, 进而导致了超导相含量的降低和织构度的破坏, 所以给体系的超导电性带来了负面的影响。另一方面, Na 掺杂相 Bi-2212 中掺入了大量的点缺陷, 这些点缺陷可以作为有效钉扎中心。因此, 通过优化 Na 掺杂 Bi-2212 的烧结工艺, 可在高场条件下获得体系性能的改善。

关键词: 高温超导材料; 化学掺杂; 涡旋钉扎机制; 临界电流密度

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