Influence of Carbon Content on Superconductivity of Bi$_2$Sr$_2$CaCu$_2$O$_x$

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Abstract

Bi$_2$Sr$_2$CaCu$_2$O$_x$ was prepared by the conventional method of solid state reaction and SHS method. The samples were annealed in different atmosphere in order to examine the influence of atmospheres on the carbon contents in the Bi$_2$Sr$_2$CaCu$_2$O$_x$ compound. The lowest carbon content in Bi$_2$Sr$_2$CaCu$_2$O$_x$ could be attended when the sample was annealed in O$_2$ at 800°C for 100 hours. The CO$_2$ in air pollute the samples and increase the carbon content in the sintering process. The critical current density of the Bi$_2$Sr$_2$CaCu$_2$O$_x$ samples will decrease with the increasing carbon contents in the samples. The impurity carbon will deposit in the grain boundary, which makes critical current density lower.

Introduction

Carbon is a common impurity in both YBa$_2$Cu$_3$O$_x$ and Bi$_2$Sr$_2$CaCu$_2$O$_x$ systems. It is well known that carbon is harmful to the superconductive properties of YBa$_2$Cu$_3$O$_x$ [1-3]. Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Bi2212) superconductor was fabricated from raw powders prepared by two standard methods; Solid-state reaction method and SHS method [4,5]. The raw materials and chemicals for sintering Bi2212 include carbonates such as CaCO$_3$ and SrCO$_3$, the incomplete decomposition of the carbonates makes carbon left in the Bi2212 compound as impurity. Because of CO$_2$ contained in the air, which will be reacted with calcium and strontium in the Bi2212 system, the carbon content in the long sintering process will remain to equilibrium value. Therefore, the carbon content can not be reduced below the equilibrium value in the sintering process in air. In the experiment, the relation between carbon content and the sintering condition (atmosphere, temperature and time of sintering) was examined. The critical current density ($J_c$) of Bi2212 samples with different carbon contents were measured by the standard 4 probe method and the relation of carbon contents and $J_c$ was studied. The optimum synthesis condition for Bi2212 superconductor was suggested.

Experimental

All reagents were obtained from Aldrich Chemical Company and used as supplied. The above chemicals for solid state reacted sample were mixed on the metal atom ratio of 2 : 2 : 1 : 2 and ground in an agate mortar for about 24 hours and dried at 200°C (Fig. 1(a)). The procedure for SHS sample was performed under a nitrogen atmosphere in the glove box. SHS reactions were carried out in air on pre-ground powders on a ceramic tile. And then grinding, pressing and sintering process was repeated several times in order to get the single phase of Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Fig. 1(b)) [6-10].

The SHSed BSCCO may be processed by the following scheme:

$3Cu + 2SrCO_3 + Bi_2O_3 + 2CaCO_3 \rightarrow Bi_2Sr_2Ca_2Cu_3O_{10-\delta}$

Where Cu is the fuel, Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ are the active fillers, and O$_2$ is a gaseous oxygen.

This method differs from other that initiation procedure takes up by termite layer which consists of exothermic mixture of Fe$_2$O$_3$ : Al = 4 : 1. The molar ratio of each reagent was chosen to confirm the desired stoichiometry in the product. Experiments were performed for Bi$_{1.8}$Pb$_{0.4}$Sr$_{2}$Ca$_{2}$Cu$_{2}$O$_{10}$ and Cu (1.8 g), PbAc (1.05 g), SrCO$_3$ (2.4 g), Bi$_2$O$_3$ (3.75 g) and CaO (1.0 g) were ground for 2 hours in a ball mill. The mixture was pressed (30 kg/cm$^2$) into 20 mm in...
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The product was ground and its phase composition and morphology of the samples were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). In this paper we noted that the variation in cooling rates affects on the crystal structure of the final composition.

SHS synthesis of HTS materials is rapid and relatively easy to perform. The major factors determining the synthesis are concentration ratios, particle size, green mixture density, briquette diameter, etc. The combustion temperature was about 1000-1100°C. The product particle size was relatively large 15-40 µm. Partial melting of the product at the high combustion temperature caused formation of the large particles. In most applications it is however desirable to produce fine powders. We found that the morphologies of all samples are also rather different, as shown in Fig. 3. Increasing the sample diameter decreases the surface/volume ratio and thus decreases the impact of the heat loss. XRD analyses of samples with diameter of 1.0 and 2.0 cm showed that the product from the pellet with the larger diameter did not contain some many impurity peaks, as for the 1.0 cm sample (Fig. 4).

Increasing the sample diameter also increased the particle size of the product phase. It is not desirable
to conduct laboratory experiments with large pellets. Controlling the cooling rate of a small diameter pellet may simulate the microstructure of a larger diameter sample and is more economical.

In the test the temperature was stable at 800°C, the ambient atmosphere was air, $\text{N}_2$ and $\text{O}_2$, and the samples were taken out of the furnace in 25 hours, 70 hours and 120 hours respectively. The relation between carbon content and treatment time under various atmosphere was shown in Fig. 5, from which it could be seen that the carbon content would attend an equilibrium value when the heat treatment time was longer than 100 hours.

Fig. 3. The evolution of structure of the products of reaction: (a) starting materials, (b) at the front zone, (c) at the product zone.

![Figure 3](image)

Fig. 4. X-ray diffraction patterns of powders made by SHS. Pellet diameter (a) 1.0 cm; (b) 2.0 cm.

![Figure 4](image)

Fig. 5. The relation between carbon content and the annealing time under different atmosphere at 800°C

![Figure 5](image)

The two carbonates $\text{CaCO}_3$ and $\text{SrCO}_3$ reacted with $\text{Bi}_2\text{O}_3$ and $\text{CuO}$ at the same time when they decomposed. The decomposition partial pressure of $\text{CaCO}_3$ is higher than that of $\text{SrCO}_3$, therefore $\text{CaCO}_3$ is decomposed easier than $\text{SrCO}_3$. At 800°C in 100 hours the decomposition of $\text{CaCO}_3$ nearly finished and the left carbon content in $\text{Bi}_2\text{212}$ is due to undecomposed $\text{SrCO}_3$. The equilibrium values are 0.05 wt.% for the treatment under $\text{O}_2$, 0.16 wt.% under air and 0.14 wt.% under $\text{N}_2$. Therefore, the equilibrium carbon content in $\text{Bi}_2\text{212}$ annealed in air and $\text{N}_2$ were 0.16 and 0.14 wt.% which were larger than that of $\text{Bi}_2\text{212}$ annealed in $\text{O}_2$ for 60 hours at the temperature from 790°C to 850°C, respectively. The different carbon contents analyzed were shown in Table 1. The relation of critical current density and carbon content was shown in Fig. 6 in which it could be seen that the critical current densities decreased with the increasing carbon contents. The sample with 0.05 wt.% carbon content was annealed in air for 24 hours, its carbon content increased to 0.16 wt.%, which was the equilibrium value of the $\text{Bi}_2\text{212}$ sample annealed in air. The increased part of carbon content in $\text{Bi}_2\text{212}$ was introduced from air. Therefore it is suggested that the sintering process of $\text{Bi}_2\text{212}$ should be taken place in the purified $\text{O}_2$. Two
samples were annealed at 860°C under air for about 60 hours and 90 hours, the carbon contents of them were 0.076 wt.% and 0.078 wt.% respectively. It means the carbon contents attended stable at 860°C over 60 hours in air. The critical current densities of the samples were 26.39 and 25.01 A/cm². Another sample with 0.84 wt.% carbon content did not show the superconductive phenomenon.

![Table 1](image)

The critical current densities of Bi2212 with the different carbon contents

| Carbon Content (wt.%) | 0.18 | 0.16 | 0.12 | 0.12 | 0.098 | 0.078 | 0.076 | 0.05 |
|----------------------|------|------|------|------|-------|-------|-------|------|
| J_c (A/cm²)          | 11.8 | 18.2 | 24.0 | 24.57| 27.0  | 26.39 | 25.01 | 38.5 |

Fig. 6. The relation of the critical current density and the carbon contents in Bi2212.

The impurity carbon may deposit in the grain boundaries, which makes the links of grain boundaries worse and it reduces the critical current density. Therefore in order to improve the critical current density of Bi2212 superconductor, the carbon content should be decreased as low as possible. In the sintering process the suitable sintering temperature, purified oxygen and reaction time should be selected to reduce the carbon content.

**Conclusions**

The carbon content of Bi2212 would be reduced in heat treatment, but it attended a stable value over a certain time. The sample with low carbon content will absorb CO_2 in air to form the carbonates in the system. Therefore, the carbon content may increase up to 0.16 wt.% which is the lowest value of carbon content in Bi2212 annealed in air at 800°C. The critical current density of Bi2212 decreased with increasing the carbon content in the system. It was estimated that the impurity carbon would be deposited in the grain boundaries of Bi2212 superconducting material and may reduce the critical current density in the system.

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