

# Influence of Carbon Content on Superconductivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ HTS

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## Abstract

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  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  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  compound. The lowest carbon content in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  could be attended when the sample was annealed in  $\text{O}_2$  at  $800^\circ\text{C}$  for 100 hours. The  $\text{CO}_2$  in air pollute the samples and increase the carbon content in the sintering process. The critical current density of the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  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.

**keywords** : carbon content,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  compound, grain boundary, critical current density

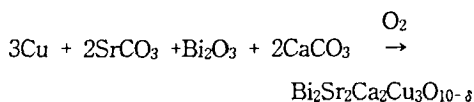
## 1. Introduction

Carbon is a common impurity in both  $\text{YBaCuO}$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  systems. It is well known that carbon is harmful to the superconductive properties of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  [1].  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  ( $\text{Bi}2212$ ) superconductor was fabricated from raw powders prepared by two standard methods; Solid-state reaction method and SHS method [2]. The raw materials and chemicals for sintering  $\text{Bi}2212$  include carbonates such as  $\text{CaCO}_3$  and  $\text{SrCO}_3$ , the incomplete decomposition of the carbonates makes carbon left in the  $\text{Bi}2212$  compound as impurity. Because of  $\text{CO}_2$  contained in the air, which will be reacted with calcium and strontium in the  $\text{Bi}2212$  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  $\text{Bi}2212$  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  $\text{Bi}2212$  superconductor was suggested.

## 2. Experiment

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  $200^\circ\text{C}$  (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  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (Fig. 1(b))[3-5]. The SHSed BSCCO may be processed by the following scheme:



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

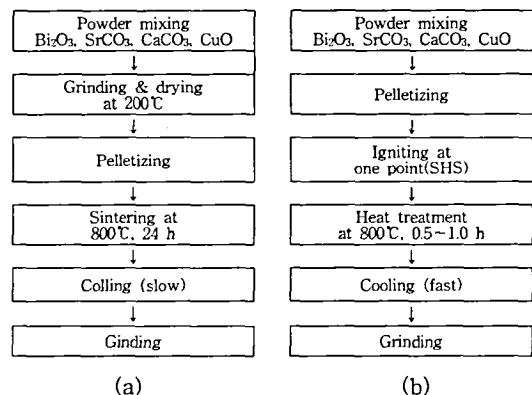


Fig. 1. Block diagram of BSCCO (2212) powder preparation by solid state reaction (a), SHS method (b).

This method differs from other that initiation procedure takes up by termite layer which consists of exothermic mixture of  $\text{Fe}_2\text{O}_3$  : Al =4:1. The molar ratio of each reagent was chosen to confirm the desired stoichiometry in the product. Experiments were performed for  $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  and Cu (1.8 g), PbAc (1.05 g),  $\text{SrCO}_3$  (2.4 g),  $\text{Bi}_2\text{O}_3$  (3.75 g) and CaO (1.0 g) were ground for 2 hours in a ball mill. The mixture was pressed ( $30 \text{ kg/cm}^2$ ) into 20 mm in diameter and 7 mm cylindrical pellet and put between 2 exothermic layers. Small holes were drilled and W-Re thermocouples inserted. They were used to measure the combustion temperature and front-propagating velocity.

The combustion velocity was determined by dividing the distance between two thermocouples by the time at which the two reacted the same temperature.

The pellet was supported on a ceramic boat and the reaction ignited by the exothermic

layers in the furnace with 700~900°C. The reaction produced an orange-yellow propagation wave that proceeded through the solid at 0.1~0.2 mm/s. The final product was a black brown combusted sample which was heated at 700~900°C during 20~60 minutes, and then, varying the cooling rate from slow cooling down in air to quenching the samples from temperature as high as the temperature of heat treatment into liquid nitrogen.

$\text{N}_2$  and  $\text{O}_2$  were chosen to be the ambient atmospheres for the annealing treatment of  $\text{Bi}_2\text{212}$ . The treatment temperature was from 800 to 850°C. The treatment time last until 120 hours, at a certain time a sample was taken out of the furnace to be checked the carbon analysis. The analysis of carbon contents were examined by the CS-244 C and S Analyzer, produced in LEC6 Company, USA the accuracy of which could be 0.001 %.

### 3. Results and Discussions

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.

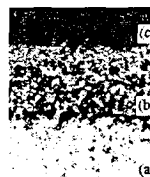


Fig. 2. The evolution of structure of the products of reaction: (a) starting materials, (b) at the front zone, (c) at the product zone.

SHS synthesis of HTS materials is rapid and relatively easy to perform. The major factors determining the synthesis are concentration

rations, 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 $\mu$ m. 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. 2. 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. 3). 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.

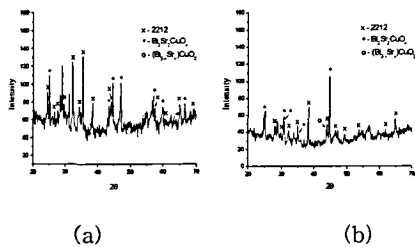


Fig. 3. X-ray diffraction patterns of powders made by SHS. Pellet diameter (a) 1.0 cm; (b) 2.0 cm.

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 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. 4. from which it could be seen that the carbon content would attend a equilibrium value when the heat treatment time was longer than 100 hours.

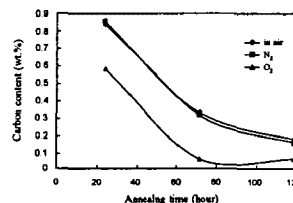


Fig. 4. The relation between carbon content and the annealing time under different atmosphere at 800°C

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 Bi2212 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 Bi2212 annealed in air and  $\text{N}_2$  were 0.16 and 0.14 wt.% which were larger than that of Bi2212 annealed in  $\text{O}_2$  for 60 hours at the temperature from 79 0°C to 850°C, respectively. The different carbon contents analyzed were shown in Table 1.

Table 1. 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
$J_c(\text{A}/\text{cm}^2)$	11.8	18.2	24.0	24.57	27.0	26.39	25.01	38.5

The relation of critical current density and carbon content was shown in Fig. 5 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 Bi2212 sample annealed in air. The increased part of carbon content in Bi2212 was introduced from air. Therefore it is suggested that the sintering process of Bi2212 should be taken place in the purified O<sub>2</sub>. 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/cmf. Another sample with 0.84 wt.% carbon content did not show the superconductive phenomenon.

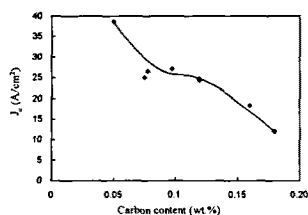


Fig. 5. The relation of the critical current density and the carbon contents in Bi2212

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.

#### 4. 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<sub>2</sub> 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.

#### Acknowledgements

This work was supported and accomplished by the KISTEP grant of M6-0011-00-0043 for int'l. joint research program.

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