Synthesis of $Bi_{2+x}Sr_2Ca_{n-1}Cu_nO_{4+2n+d}$ compounds by SHS

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Abstract

BSCCO (2223) compound which has the highest temperature of transition to the superconducting state in the homologous series considered is synthesized by SHS. The method exploits self-sustaining solid-flame combustion reactions which develop very high internal material temperatures over short periods. This report introduces the SHS method and its advantages and discusses its application in the synthesis of superconducting materials.

Key Words : BSCCO, superconducting state, SHS, self-sustaining solid-flame combustion reactions

1. Introduction[1]

There are basically two superconducting phases of interest in the BSCCO system. One is the low temperature T_c (80 K), $Bi_2Sr_2CaCu_2O_{8+x}$ (2212) phase and the other is the high temperature T_c (110 K), (2223) phase [1-2]. The importance of proper characterization is paramount in determining optimum conditions for processing of any ceramic compound. An understanding of kinetics and dynamics of these processes should yield insights into how J_c can be maximized. There are two standard methods being used for preparating powders of copper ceramic superconductors:

Solidstate reaction method and Coprecipitation method. First method involves mixing of carbonate or oxide powders followed by ball milling. The length of this process depends on homogeneity required but usually varies from 2 to 10 hours. This is repeated until the desired composition is obtained. In the second method the nitrates of the individual constituent are used. They are mixed in the correct proportion in water and heated. The powders produced by either of the two methods are tested for the uniformity, stoichiometry, CO_2 for the carbonate powders. The validity of these studies is based primarily on the assumption that the phases observed in quenched samples are representative of the equilibrium conditions at high temperature. May be this assumption is valid for simple systems, but for complicated as BSCCO system may not be valid.

Self-propagating high temperature synthesis is a process that enables the rapid formation of the materials by utilizing the energy given out in a very exothermic solid-state reaction [3-4]. SHS reactions are accompanied by rapid heating and cooling and often proceed by the passage of a synthesis wave from the point of ignition throughout the solid compact. We have an interest in the synthesis of superconductors by SHS [4]. In this work we study the effect of SHS synthesis on the bismuth-containing HTS with the purpose of optimizing the technology of preparation of 2212 and 2223 composition compounds in the BSCCO system.

2. Experimental part

All reagents were obtained from Aldrich Chemical Company and used as supplied. All procedures as weighings and grindings were performed under a nitrogen atmosphere in the

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glove box. SHS reactions were carried out in air on pre-ground powders on a ceramic tile. An SHS process is characterized by high temperatures and high velocity of the combustion front propagation. The process may be represented by the following scheme:

$$A_{solid} + B_{solid} + C_{solid} + D_{solid} \xrightarrow{gas} ABCD_{solid} + Q$$

i.e. in the combustion wave there proceeds a chemical reaction in the mixture of initially solid products with heat evolution, Q.

On practice we had

$$3Cu + 2SrCO_3 + Bi_2O_3 + 2CaCO_3 \xrightarrow{O_2} Bi_2Sr_2Ca_2Cu_3O_{10-\delta}$$

Where Cu is the fuel, Bi_2O_3 is an active filler, and O_2 is a gaseous oxygen.

This method differs from other that initiation procedure takes up by thermite layer which consists of exothermic mixture of Fe_2O_3 : Al = 4 : 1. The molar ratio of each reagent was chosen to conform to the desired stoichiometry in the product. Seria N1 was performed for BSCCO (2212) phase and Cu (1,66 g), $SrCO_3$ (2,6 g), Bi_2O_3 (4,04 g) and $CaCO_3$ (1,7 g) were ground for 1 hour in a ball mill. Seria N2 was performed for Bi1.8Pb0.4Sr2Ca2Cu3O10 and Cu (1,8 g), PbAc (1.05 g), $SrCO_3$ (2,4 g), Bi_2O_3 (3,75 g) and CaO (1,0 g) were ground for 1 hour in a ball mill. The mixture was pressed (30 kg/㎠) into 20 ㎜ in diameter and 7 ㎜ cylindrical pellet and put between 2 exothermic layers. Small holes were drilled and W-Re thermocouples inserted. The pellet was supported on a ceramic boat and the reaction ignited by the exothermic layers in the furnace with 700-800℃. This produced an orange-yellow propagation wave that proceeded through the solid at 0.1-0.2 ㎜/s (Fig. 1). This produced a black brown combusted sample which was heated at 700-800℃ during 20-40 minutes and then varying the cooling rate from slow cooling in air to quenching the samples from temperature as high as the temperature of heat treatment into liquid nitrogen.

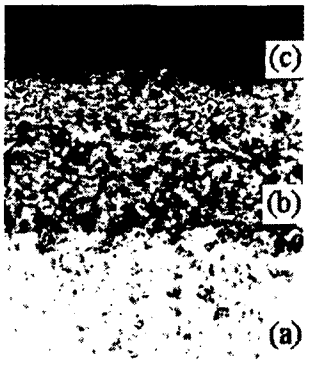
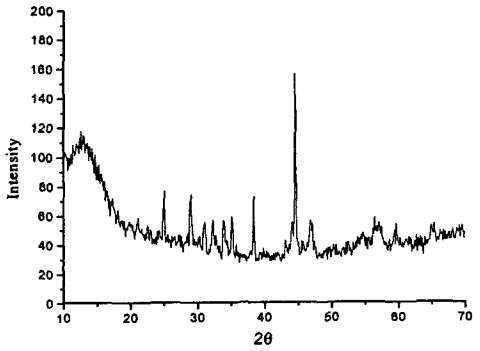


Fig. 1. The evolution of structure of the products of reaction.
(a) starting materials, (b) at the front zone, (c) at the product zone.

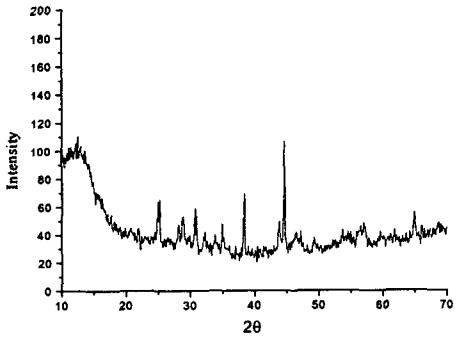
The phase composition and morphology of the samples were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). In this paper we noted that the variation in cooling rates affects on the crystal structure of the final composition.

3. Results and discussion

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. 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 ㎝ showed that the product from the pellet with the larger diameter did not contain some many impurity peaks, as for the 1.0 ㎝ sample (Fig. 2).



(a)



(b)

Fig. 2. X-ray diffraction patterns of powders made by SHS.
Pellet diameter (a) 1.0 cm, (b) 2.0 cm.

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.

The product microstructure (Fig. 3) consisted of 2212 and non-superconducting phases, mainly $CaPbO_4$ and CuO.

The inhomogeneity was due to the short time during which the sample was at a high temperature. Because of the significant heat loss, the rapid pellet cooling did not enable complete homogenization.

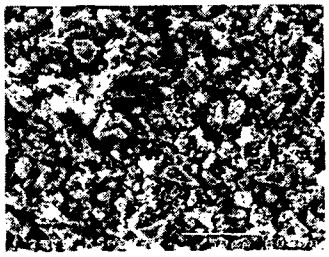


Fig. 3. Microstructure of 2.0 cm diameter pellet made by SHS.

Pre-heating the green pellet enhanced the homogenization of the product by increasing the combustion temperature as

$$T_c = T_0 + (-\Delta H)C_0 / c_p(T)\rho ;$$

where T_0 is the initial temperature, $-\Delta H$ the average heat of the reacti on, C_0 the concentration of the limiting reactant, the conversion, $c_p(T)$ the mean specific heat. Pre-heating is often used to combust low exothermic mixtures, which are not combustible at room temperature. Pre-heating a sample in our experiments had two effects. First it increased the combustion temperature to 1100-1200℃ and prolonged the exposure time of the combusted sample to high temperatures. Both effects increased the homogeneity of the product. A black-scattered electron image of the microstructure of this pellet is shown in Fig. 4.

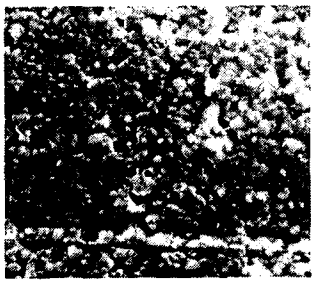


Fig. 4. Black-scattered electron image of BPSCCO sample subjected to controlled cooling.

It was known [5] who investigated phase regions and kinetics of $(BiPb)_2Sr_2Ca_2Cu_3O_x$ formation and found 2223 phase formed between 810 ° and 837 ℃.

4. Conclusions

Formation of by SHS reaction is a complex process with several intermediate reactions occurring at different combustion zones at different initial temperatures. The final product started to form in the post-front zone and its final microstructure and composition was determined in the final products and cooling zone. SHS method enables a simple synthesis without expensive equipment and is time and energy efficient. The impurity, non-superconducting phase, would be reduced and changed to superconducting phase by further heat treatment during 20-40 minutes.

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