Peculiarities of SHS and Solid State Synthesis of $ReBa_2Cu_3O_{7-x}$ Materials

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Abstract

The peculiarities of using Self-propagating High-temperature Synthesis (SHS) and solid-state phase synthesis for production of high temperature superconductor materials were discussed. Oxide superconductors with general formula of $ReBa_2Cu_3O_{7-x}$ (Re=Y, Sm) have been made by using barium oxide initial powder instead of traditional barium carbonate. Phenomena observed during the grinding of the reactants mixture are presented. Mechano-chemical activation – as a pre-treatment of the reactants mixture – strongly influences the kinetic parameters, the reaction mechanism, and the composition and structure of the final product.

Key Words : Self-propagating High-temperature Synthesis (SHS), $ReBa_2Cu_3O_{7-x}$,,Oxide superconductors, SHS propagation, Combustion velocity

1. Introduction

Synthesis of oxide materials provides an excellent case study of the contribution of solid-state chemists to materials synthesis. Although tailoring oxides of the desired structure and properties remains the main goal of solid-state chemistry and materials science, it is not always possible to do so. One can evolve a rational approach to the synthesis of solids, but there is always the element of surprise encountered not so uncommonly.

In all cuprate superconductors the critical temperature depends on the oxygen content, which can be adjusted with the temperature and the oxygen partial pressure during heat treatment. The conditions during powder synthesis are therefore of crucial importance for the resulting physical properties of superconducting wires and bulk

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material.

The most promising materials for the bulk application are oxide superconductors with general formula of $ReBa_2Cu_3O_{7-x}$ [1]. To develop the optimum microstructure for samples it is necessary to have an understanding of how these processes affect the microstructure and hence the properties of ceramic superconductors.

Taking into account on one hand, the fact that the quality of the precursor is of prime importance to get the desired properties for a given application and on the other hand, the economically point of view, different processes for powder production have been studied. In this way a comparative study of the kinetics and phase formation of the ReBCO between *solid-state synthesis* and *SHS* methods have been carried out. The same nominal compositions Y(123) and Sm(123) have been used for two methods, because a small variation of the starting composition may result in various phase equilibrium.

The peculiarities of using *Self-propagating High-temperature Synthesis* and *solid-state phase synthesis* for production of high temperature superconductor materials were also discussed. Phenomena of mechano-chemical activation observed during the grinding of the reactants mixture were presented. Mechano-chemical activation – as a

pre-treatment of the reactants mixture - strongly influences the kinetic parameters, the reaction mechanism, and the composition and structure of the final product.

2. Experimental Procedure

The standard process for synthesizing high-T_c ceramic superconductors involves mixing oxides of the constituent elements, followed by subsequent heat treatments at temperatures of 900~1100℃, when the materials could be synthesized through the solid-state reaction known as thermal sintering. However, the volume fraction of the resulting superconducting phase in the oxides thus prepared generally amounts to only about 20~30%, indicating the difficulty in achieving a homogeneous single phase material [2], especially using $BaCO_3$. In this case the mixed powder is pre-calcined in an electric furnace at 880~940℃ for about 12 hrs. in an oxygen or air atmosphere.

Oxide superconductors with general formula, $ReBa_2C_3O_{7-x}$, have been made by using barium

Oxide initial powder instead of traditional barium carbonate. Appropriate amounts of Y_2O_3 (or Sm_2O_3) CuO, BaO are mixed and ground thoroughly. The calcined powder was ground and then pelletized into a disk form. The pellets were sintered at 890~920℃ for 12 h. under oxidizing atmosphere and then cooled down slowly to room temperature. It is very important to cool down slowly in an oxygen or air atmosphere, especially passing through the 400~600℃ region, during 2 hours at least. This conventional process is an energy intensive and time-long process. Alternative processing route of SHS has been attempted to solve such problems. All the preparing procedures were conducted in a nitrogen-filled glove box. Reactions were typically conducted in air on a supporting ceramic substrate with additional mixture of BaO + CuO and initiated by the application of chemical thermite (Al + Fe_2O_3) at 800℃. Reagents of Cu (10~15 μm), Re_2O_3 and BaO_2 were purchased from Aldrich Chemical Co. and used as supplied. Powders were mixed in a Spex mill for 1 hour.

The mixed powder was compacted into a disk-shaped pellet under 50 MPa pressure. The green pellet was 10 and 20 mm in diameter and 28 and 46 mm in height. The pellet was then placed in a reaction chamber (Fig.2) under atmospheric pressure. Initiated at 800 ℃ reaction of thermite produced a self-propagating reaction of 0.5~2.0 mm /s velocity. The combustion temperature was measured using (Pt30%Rh-Pt6%Rh) thermocouple inserted into the pellet and was recorded by a computer data acquisition system. The maximum temperature reached in the reactions was ranged between 1100 and 1300℃.
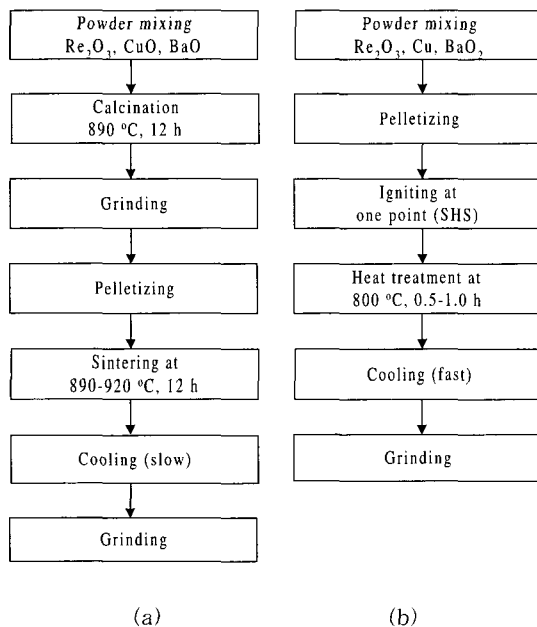

Powder mixing Re₂O₃, CuO, BaO	Powder mixing Re₂O₃, Cu, BaO₂
Calcination 890 ℃, 12 h	Pelletizing
Grinding	Igniting at one point (SHS)
Pelletizing	Heat treatment at 800 ℃, 0.5-1.0 h
Sintering at 890-920 ℃, 12 h	Cooling (fast)
Cooling (slow)	Grinding
Grinding	

(a)　　　　　　　(b)

Fig. 1. Block diagram of ReBCO (123) powder preparation by solid-state reaction (a), by SHS method (b). Calcination must be done in an oxidizing atmosphere.
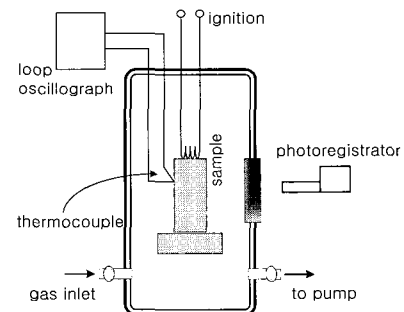

Fig. 2. SHS reaction chamber. (constant pressur bomb)

3. Results and Discussion

3.1 Peculiarities of solid state synthesis of $ReBa_2Cu_3O_{7-x}$ materials

During the first few years, solid-state amorphous techniques received much attention. Yamada Y. et al [2] considered this technique to be suitable not only for synthesizing amorphous powders but also for preparing and mixing multi-component materials, reacted at the atomic level through solid-state diffusion.

In the present work, we performed high-energy ball milling for a mixture of metal oxide powders under various conditions. Benefits offered by mechanical activation in preparing fine dispersed materials are well recognized [3].
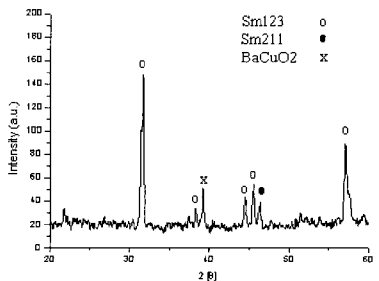
(a)

(b)

(c)
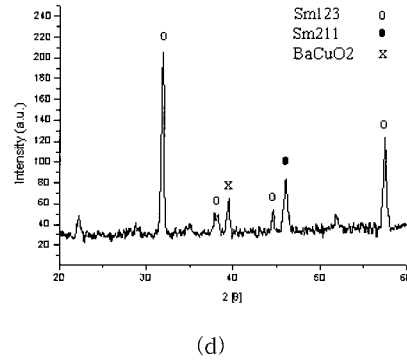
(d)

Fig. 3. X-ray analysis of solid-state reaction synthesis of Y_{123} and Sm_{123} powders. (a) Y123 from $BaCO_3$, (b) Y123 from BaO, (c) Sm123 from $BaCO_3$, (d) Sm123 from BaO.
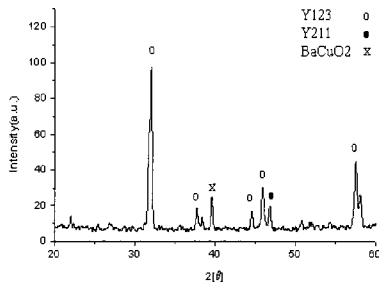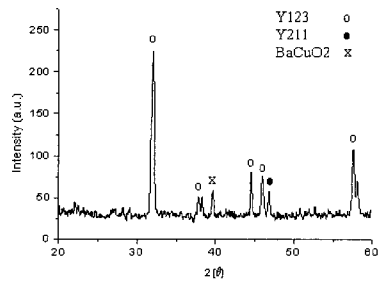
Whenever mechanical activation was employed at an early synthesis stage, the proper choice of the original components is very important. Barium carbonate, $BaCO_3$, is an example of improper choice [4,5] in the synthesis of ReBCO (Fig. 3a, 3c). Particles of these compounds diminish in size in the course of mechanical grinding (with ordinary activation doses) rather than becoming amorphous, as do many other materials.

This is apparently attributable to the strong bond between atoms in the lattice, which is supported by the high melting point of this compound. It was found, that the mechanism of compound formation either remains identical to the ordinary one, i. e. synthesis involves the green Y_2BaCuO_5 phase, or proceeds concurrently through the blue $Re_2Cu_2O_5$ and green Re_2BaCuO_5 phase. Transition of the green phase to $ReBa_2Cu_3O_x$ is known to be hindered, therefore high values of T_{sint} and τ_{sint} are required to form the end product. The mechanism changes drastically when barium oxide BaO is chosen as the starting material [6].

This compound easily becomes amorphous in the course of grinding and enters into reaction with CuO producing cuprates and leaving unchanged Re_2O_3, which can hardly be made amorphous. Hence, $ReBa_2Cu_3O_x$ is produced via the following reaction;

$$4BaCuO_2 + Re_2O_3 + 2CuO = 2ReBa_2Cu_3O_x + kO_2$$

(1)
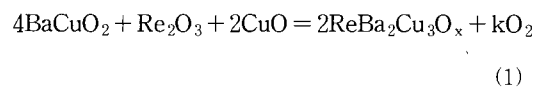
In which participation of the green phase in synthesis is completely ruled out. This reaction pathway not only provides the highest phase homogeneity (Fig. 3b, 3d), but also significantly reduces the time (up to 12-40 hours) and lowers the temperature of synthesis of the desired compound [7].

3.2 Peculiarities of SHS synthesis $ReBa_2Cu_3O_{7-x}$ materials

SHS method is based on the exothermic interaction of two or more chemical elements or compounds, which proceeds in oriented combustion regime. SHS reactions are accompanied by rapid heating and cooling processes. It often proceeds by the passage of a synthesis wave away from the ignition point throughout the solid compact. Once initiated, highly exothermic reactions can become self-sustaining and will propagate through the reactants mixture in the form of a combustion wave. The process may be represented by the following scheme;

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

(2)
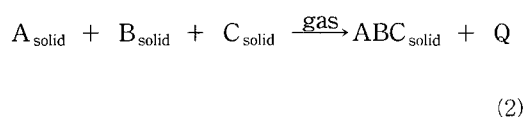
i. e. in the combustion wave there proceeds a chemical reaction in the mixture of initially solid products with heat evolution, Q. On practice we had;
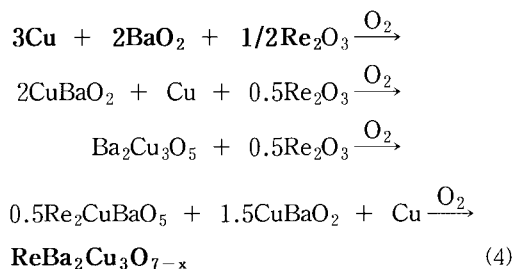
$$3Cu + 2BaO_2 + 1/2Y_2O_3 \xrightarrow{O_2} YBa_2Cu_3O_{7-x}$$

(3)
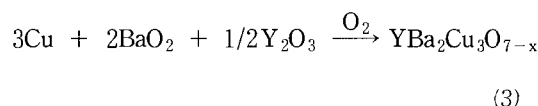
Where Cu is solid fuel, BaO_2 is solid oxidant, Y_2O_3 is active filler, and O_2 is gaseous oxygen. Two groups of parameters should be outlined. One of them characterizes the initial reactants mixture (chemical composition, shape and size of reactants particles, and shape, size, and density of samples). The other characterizes the combustion condition (composition and pressure of the environment, initial temperature of the compact, the method and intensity of combustion initiation, or additional external effects). It should be noted that the regularities and mechanism of combustion are strongly dependent on the melting points of the components. In our experiments one of the components (BaO_2) suffers melting during the

synthesis.

A stoichiometric mixture exhibits the highest velocity of propagation and the combustion being steady state, i. e. the velocity of the SHS front propagation along the sample is the same at any moment. It was founded the combustion velocity in the ReBCO system is weakly dependent on the sample thickness. This is explained by high heat of the reaction between melted phase and yttrium oxide, which exceeds much the heat loss level even at small diameters of the sample. It was stated the combustion velocity does not depend on the pressure of the oxygen, under which the process is carried out. It was noted the decrease in the combustion velocity with the increase in the size of copper particles. It is of interest that the combustion velocity is practically constant down to 100 μm.

The limiting reagent in the reactions was oxygen which had to diffuse into the reacting powders. The specific feature of our system is as follows; one portion of the oxidant is put into the blend in the solid state (for example, oxygen contained in barium peroxide), the other portion is involved by filtration forms the outer sphere, since the combustion is carried out under oxygen. Whenever both components of the starting mixture (Cu, BaO_2) have low melting points and, hence, one can anticipate a significant reduction of the temperature and time of double-compound formation. $ReBa_2Cu_3O_x$ exemplifies this inference. Being low-melting compounds, copper and barium peroxide form readily the amorphous phase in the course of mechanical activation, therefore in the ternary Re_2O_3-BaO_2-Cu system they interact first, and only later on the product of their interaction reacts with Re_2O_3. Then we tray to explain the mechanism of $ReBa_2Cu_3O_{7-x}$ phase formation in the SHS regime;

$$3Cu + 2BaO_2 + 1/2Re_2O_3 \xrightarrow{O_2}$$

$$2CuBaO_2 + Cu + 0.5Re_2O_3 \xrightarrow{O_2}$$

$$Ba_2Cu_3O_5 + 0.5Re_2O_3 \xrightarrow{O_2}$$

$$0.5Re_2CuBaO_5 + 1.5CuBaO_2 + Cu \xrightarrow{O_2}$$

$$ReBa_2Cu_3O_{7-x}$$

(4)

The leading stage of combustion is the formation

of barium cuprates. This stage includes spreading of the BaO_2 melt along the surface of metallic copper, the latter oxidation by oxygen of the melt, compensation of oxygen loss in the melt by its consumption from the gas phase. The formation of Re-containing phases occurs at later stages than that of barium cuprates does. All of the major peaks were found to match with the standard peaks of $YBa_2Cu_3O_{7-x}$, indicating the formation of YBCO(123) of rhombic structure a=3.824; b=3.889; c=11.698 via the SHS reaction (Fig.4).

We compare structure with powders synthesized by solid phase reaction: a=3.827; b=3.884; c=11.650.
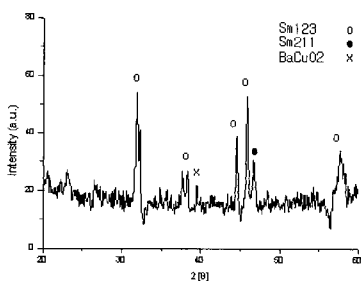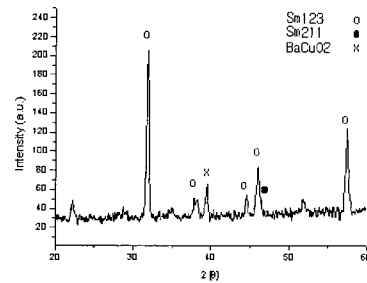
In processing of HTS materials via SHS, the
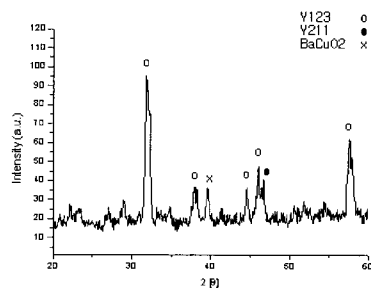
(a)
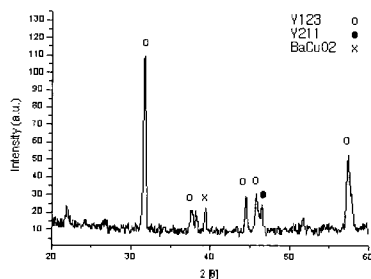
(b)

(c)

(d)

Fig. 4. X-ray analysis of YBCO (a, b) and SmBCO (c, d) powders by SHS; heat treated at 800 ℃ after 20 min. (a, c), and after 40 min. (b, d) (● : 211 phase, X : Liquid phase)

reaction products were found to include the aimed phase, but also the intermediate phases and the unreacted cores.

The final $ReBa_2Cu_3O_{7-x}$ phase crystallizes from the melt solution as tiny crystals. Figure 5a, 5b show results for the samples melted by SHS at 1100℃, heat-treated at 800℃ during 20~40 minutes, then cooled fast to room temperature.

The intensities of the small 211 peaks decreased slowly with time as the 211 reacted with the liquid to form 123. We suppose that due to thesmall geometry of samples this time delay is not likely a result of thermal lag. Other reasons were postulated which seemed more likely: 1) the oriented 123 grains were initially forming under the liquid phase and therefore were not immediately observed. 2) The 211 grains required sufficient time to dis- solve into the liquid phase, thus allowing the stoi- chiometry to approach that of the 123 composition for significant growth of the textured grains. The 211 crystals tie up the rare-earth metal oxide required in the melt for 123 growth. The practical performance of a ceramic component, the micro- structure of the ceramic, and powder behavior during processing are strongly dependent on the physical and chemical characteristics of starting powders. We know that in the manufacture of advanced ceramic components, detailed in-formation on powder characteristics is required to achieve reproducibility and cost competitiveness.

In the measurement of particle or agglomerate size distribution, the major distinction is that agg-
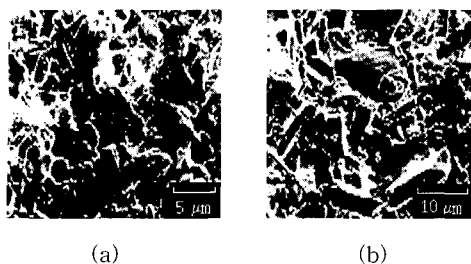
(a)   (b)

Fig. 5. Micrographs of YBCO powder structure:
(a) as prepared after SHS and (b) calcined
at 800℃ in the oxygen flow.

lomerates are made of primary particles. Microstructure of fine 0.1~5 μm particles deposited on thin membranes are examined (Fig.5).

3.3 Technological consequences of the specific SHS mechanisms

Thus, from the discussed before the specific reaction mechanisms on SHS permits us to:
1. synthesize complex compounds,
2. synthesize compounds from reactants differing widely in their melting points,
3. produce complex oxides having a rather homogeneous distribution of the components.

It is true that these goals can also be reacted by more conventional methods, but at high levels of their sophistication involving more time consuming operations. Therefore, already from this point of view a use of SHS is that it can help to simplify the technologies and make them more time-efficient in comparison with the conventional ones. We may say, that additional advantageous features of SHS-derived powders contribute to the simplification of processing. Namely a high powder purity, a small and rather uniform particle size of the powders.

4. Conclusions

One of the most important tasks of modern technology and science faces is to compare the various technological processes and determine more efficient fields of their application. The same problems can be solved by modern technologies that are based on powder metallurgy. plasma techniques, combustion, etc. It is no surprise, therefore, that there is competition between technologies. We are not sure whether we use the most efficient one. Because SHS method is among the most up-to-date technologies,

we look ahead with confidence.

The use of cheap chemical energy instead of electrical energy, fast bulk self-heating rather than slow heating through the substance surface, and simple devices rather than complicated high-temperature ones are features of the progressive technological principles of the SHS process. Clearly, SHS is an alternative to the traditional approaches, but it should be noted, however, that SHS products differ from their furnace counterparts in purity and structure.

Acknowledgments

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