Peculiarities of SHS and solid state synthesis of ReBa$_2$Cu$_3$O$_{7-x}$ 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 are discussed. Oxide superconductors with general formula ReBa$_2$Cu$_3$O$_{7-x}$ (Re= Y, Yb, Sm, Nd) have been made with using barium oxide initial powder instead of traditional barium carbonate. X-ray powder diffraction showed a single phase orthorhombic perovskite structure was produced in all reactions. Phenomena observed during the grinding of the reactant mixture are presented. Mechano-chemical activation - as a pretreatment of the reactant 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, solid state phase synthesis, oxide superconductors, mechano-chemical activation.

I . Introduction

The most promising materials for the bulk application are oxide superconductors with general formula ReBa$_2$Cu$_3$O$_{7-x}$ (Re = Y, Yb, Sm, Nd). The properties, which are of high interests, are the levitation force and the trapped magnetic field. The weak links and the pinning force for the magnetic flux in the bulk material limit these. Weak links can be avoided by growing large grains, which can be achieved by different methods [1]. To develop optimum microstructures for samples it is necessary to have an understanding of how these processes affect the microstructure and hence the properties of ceramic superconductors. This study was undertaken to gain a better understanding of the mechanism of the textured 123 formation. The peculiarities of

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using Self-propagating High-temperature Synthesis (SHS) and solid state phase synthesis for production of high temperature superconductor materials are discussed. Phenomena of mechano-chemical activation observed during the grinding of the reactant mixture are presented. Mechano-chemical activation - as a pretreatment of the reactant mixture - strongly influences the kinetic parameters, the reaction mechanism, and the composition and structure of the final product.

II. 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 900-1,100 °C, when the material is synthesized through the solid state reaction known as 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 BaCO₃. In this case the mixed powder is pre-calcined in an electric furnace at 880-940 ℃ for about 12 h in an oxygen or air atmosphere.
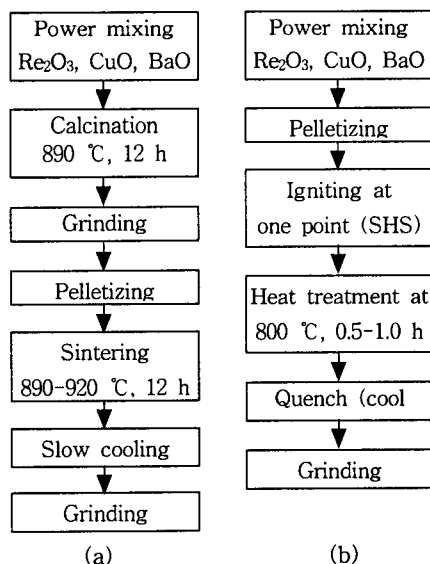
Power mixing Re₂O₃, CuO, BaO	Power mixing Re₂O₃, CuO, BaO
Calcination 890 ℃, 12 h	Pelletizing
Grinding	Igniting at one point (SHS)
Pelletizing	Heat treatment at 800 ℃, 0.5-1.0 h
Sintering 890-920 ℃, 12 h	Quench (cool
Slow cooling	Grinding
Grinding	
(a)	(b)

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.

Oxide superconductors with general formula $LnBa_2C_3O_{7-x}$ (Ln = Y, Yb, Sm, Nd) have been made with using barium oxide initial powder instead of traditional barium carbonate. Appropriate amounts of Y_2O_3 or (Yb_2O_3, Sm_2O_3, Nd_2O_3) CuO, BaO are mixed and ground thoroughly. The calcined powder is ground and then pelletized into a disk form. The pellets are sintered at 890-920 ℃ for 12 h under oxidizing atmosphere and then cooled slowly to room temperature. It is very important to cool slowly in an oxygen or air atmosphere, especially passing the 400-600 ℃ region, for at least 2 h. These conventional processes are an energy intensive and time-long process. Alternative processing route SHS has been attempted to decide the problem. All preparations were conducted in a nitrogen-filled glove box. Reactions were typically conducted in air on a supporting ceramic tile with additional coating from (BaO + CuO) mixture and initiated by the application of chemical termite (Al+ Fe₂O₃) at 800 ℃. Reagents Cu (10-15 μm), Re₂O₃ and

BaO₂ were purchased from Aldrich Chemical Co. and used as supplied. Powders were mixed in a Spex mill for 1 h. The mixed powder was compacted in a steel die 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 atmosphere pressure. Initiated at 800 ℃ reaction of thermite produced a self-propagating reaction of 0,5-1,5 mm/s velocity [3]. The combustion temperature was measured using a C-type thermocouple inserted into the pellet and was recorded by a computer data acquisition system. The maximum temperature reached in the reactions was ranged between 1,100 and 1,300 ℃.
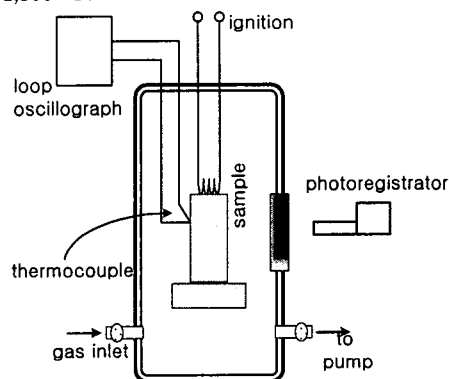

Fig.2. SHS reaction chamber (constant pressure bomb)

XRD analysis of the resulting powder has been prepared by SHS and solid state synthesis indicated a very quality diffraction pattern for the orthorhombic 123 phase with no detectable impurity phases.

III. Results and discussion

a) Peculiarities of solid state synthesis of ReBa₂Cu₃O₇₋ₓ materials

During the first few years, solid-state amorphization techniques received much attention. Particularly, it has been reported that an amorphous phase can be obtained relatively easily by ball-milling the constituent elemental powders. 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. Whenever mechanical activation is employed at an early synthesis stage, of great importance is the proper choice of the original components. Barium carbonate $BaCO_3$ is an example of improper choice in the synthesis of ReBCO (Fig.3a).
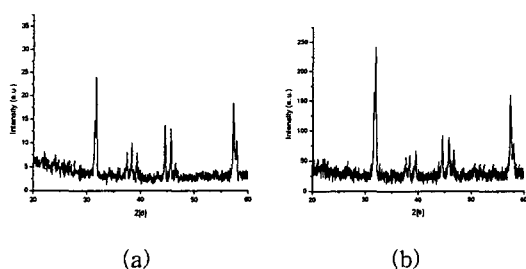

(a)   (b)

Fig.3. X-ray analysis of solid state reaction
synthesis of Y(123) powders.
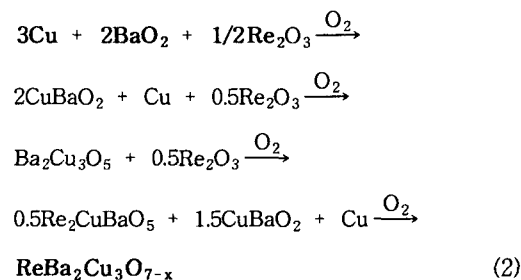(a) $BaCO_3$, (b) BaO as starting materials.

Particles of these compounds diminish in size in the course of mechanical grinding (with ordinary activation doses) rather than become 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 Tsint and tsint are required to form the end product. The mechanism changes drastically when barium oxide BaO is chosen as the starting material [4]. 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

$$4BaCuO_2 + Re_2O_3 + 2CuO$$
$$= 2ReBa_2Cu_3O_x + kO_2 \qquad (1)$$
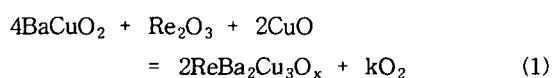
in which participation of the green phase in synthesis is completely ruled out. This reaction pathway not only provides the highest phase homogeneity (Fig.3b), but also significantly reduces the time (up to 12-40 h) and lowers the temperature of synthesis of the desired compound [5].

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

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 explain the mechanism of $ReBa_2Cu_3O_{7-x}$ phase formation in the SHS regime:

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

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

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

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

$$ReBa_2Cu_3O_{7-x} \qquad (2)$$

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, which is caused by the peculiarities of the microstructure of the reacting medium (Fig.4). The final $ReBa_2Cu_3O_{7-x}$ phase crystallizes from the melt

solution as tiny crystals. Figure 4a, 4b show results for the samples melted by SHS at 1,100 ℃, heat-treated at 800 ℃ during 20-40 minutes, then cooled fast to room temperature.
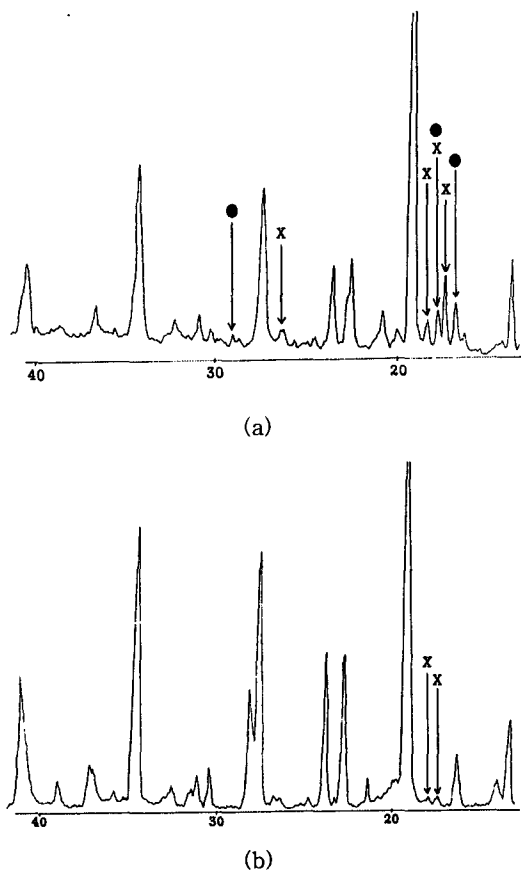

(a)

(b)

Fig.4. X-ray analysis of SmBCO powders; (a) after 20 minute heat treatment at 800 ℃, (b) after 40 minutes. (X)-211 phase ; ● - L phase

The intensities of the small 211 peaks decreased slowly with time as the 211 reacted with the liquid to form 123. Due to the small geometry of these 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 dissolve into the liquid phase, thus allowing the stoichiometry to approach that of the 123 composition for significant growth of the textured grains. Thus the 211 crystals tie up the rare-earth metal oxide required in the melt for 123

growth. To confirm these speculations, quenching samples on the microscope stage at various points during the first 10-20 minutes will perform additional experiments.

IV. Conclusions

Among the processes, the SHS route has attracted much research interest recently, but it should be noted, however, that SHS products differ from their furnace counterparts in purity and structure. Their application therefore, requires different processing conditions.

The exact nature of the nucleation and growth mechanism is not fully understood. Furthermore, the structure of as-grown 123 is known to be a strong function of the cooling rate. At high cooling rates there is a distinct change in the nucleation and growth processes. In turn, the critical current density of melt-processed 123 is directly dependent on its microstructure.

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