Structural and transport properties of superconducting ceramics $Bi_2Sr_2CaCu_2O_{8+d}$

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Abstract

The influences of the conditions of the firing and successive thermal treatments on the final quality of samples of superconducting ceramics $Bi_2Sr_2CaCu_2O_{8+d}$ are studied in this work. Different initial calcination methods and different starting mixtures of the compounds Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO have been tested. Structural analysis has been by means of X-ray Diffraction and scanning electronic microscopy. The critical transition temperatures T_c have been determined by resistivity versus temperature measurements. The samples analyzed present a pure and textured Bi-2212 phase. The results confirm also that, during sintering, the 2201 phase begins to appear after 10 h and disappears after 72 h. Long sintering time improves the density of the sample. Transport measurements results show that superconducting properties are mainly dependent of the density of the sample, its texture and the relative grain growth. Increasing the sintering time increases the onset of the superconducting transition T_c^{on}. The texture improves the superconducting transition width. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bi-2212 phase; Superconducting ceramics; Bi–Sr–Ca–Cu–O system; HTSC

1. Introduction

Since their discovery [1] superconducting oxides had a great importance for the use of their high-transition temperature. The Bi-2212 phase is one of these superconducting materials. Having an 80 K minimum transition temperature (T_c is higher with better oxygenation) [2,3], this phase can be obtained by various methods as the solid-state reaction [4], the oxide powder in tube method [5], the melt textured growth (MTG) [6], the citrate method [7] and the isothermal partial melting method [8]. The final quality of the sample and its superconducting properties are directly influenced by the method used. For example, the transition width of a sample obtained by a solid state reaction is larger than the one of a sample obtained by an MTG method. The texture obtained by the MTG method is better. In the solid state reaction, increasing the time of sintering [9] may reduce the transition width of the sample.

We have prepared samples of Bi-2212 phase using the solid state reaction with different conditions of calcination and sintering. The samples have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and measurement of resistivity versus temperature $\rho(T)$.

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2. Experiment

Using the solid state reaction, samples have been prepared with high purity (>99%) Bi_2O_3, $CaCO_3$, CuO and $SrCO_3$ (minimum 98%). Weighted in a stoichiometric proportion of Bi/Sr/Ca/Cu = 2/2/1/2, the mixture was firstly ground in an agate mortar. Some samples were prepared with a non-stoichiometric proportion. The powder was then calcined during 10 h at a temperature between 800°C and 835°C. The obtained powder was, after that, ground and pressed in pellet shape with a pressure of $2 t/cm^2$. The samples were sintered during 10–72 h at temperatures between 820°C and 835°C (Table 1).

At each step of the preparation, the samples were analyzed by XRD using K_α radiation of copper ($\lambda_{CuK\alpha} = 1.54060$ Å). Identification of the phases was made with help of ASTM data file [10]. Microstructural observations were made with a PHILIPS XL30 SEM using a tilt of $0°$.

Resistivity versus temperature $\rho(T)$ was measured with a classical four-lead technique using an AC current with constant amplitude. These measurements were made in a homemade apparatus working from room temperature until liquid nitrogen temperature (77 K).

3. Results and discussion

3.1. XRD

Fig. 1a shows the XRD spectrum of sample 1 after calcination. The Bi-2212 phase is dominant. We note the presence of the weak peak corresponding at $2\theta = 25.2°$ to $SrCO_3$ due to its long

Table 1
Sample preparation conditions

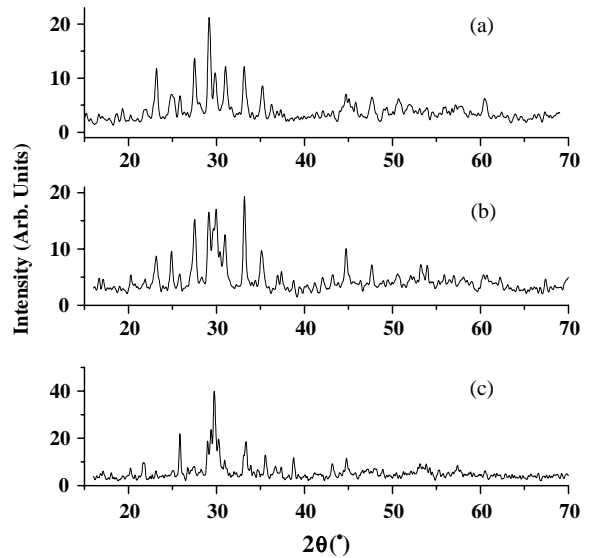| Sample	Calcination	Sintering
1	810°C/15 h	840°C/15 h
2	835°C/10 h	835°C/10 h +810°C/10 h
3	835°C/10 h (stoichiometric)	810°C/25 h
4	835°C/10 h (stoichiometric)	820°C/60 h
5	835°C/10 h (stoichiometric)	820°C/72 h

Fig. 1. XRD Spectrum of the powders calcined at: (a) 810°C during 15 h; (b) 835°C during 10 h; and (c) 835°C during 10 h (stoichiometric composition).

time of decomposition [11] and the one at $2\theta = 29.8°$ corresponding to the 2201 phase and due to the difficulty of separation of these phases during calcination. Fig. 1b shows the XRD spectrum of sample 2 after calcination. Here again, the Bi-2212 phase is obtained. Fig. 1c shows the XRD spectrum of samples 3–5 after calcination. The formula of the obtained phase here is $Bi_2Sr_{2.5}Ca_{0.5}Cu_3O_x$. The excess of strontium and copper and the deficiency of calcium are a consequence of the different reactivities of the starting materials.

The XRD spectrum of sample 1 after sintering is shown in Fig. 2a. The intensity of the 2201 phase peak is negligible compared to the same one after calcination. The 2212 phase peaks have increased and the $(0 0 l)$ peaks are dominant. This fact indicates a preferential orientation, as it is current in the Bi-2212 compound [12]. Fig. 2b shows the XRD spectrum of sample 2 after sintering. We note the fact that the intensities have increased, indicating that a second sintering favors an increase of the grain size. Fig. 2c shows the XRD spectrum of a sample made from the same calcinated powder as sample 1 but for which the first sintering is made at 810°C during 15 h.
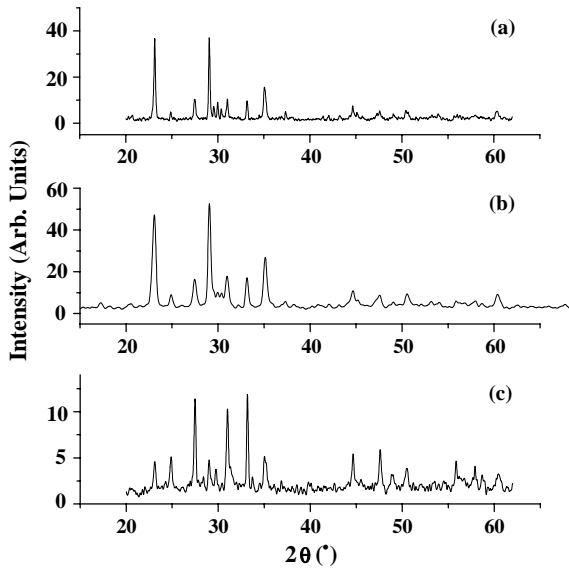
Fig. 2. XRD Spectrum of the pellets sintered at: (a) 840°C/15 h; (b) 835°C/10 h + 810°C/10 h; and (c) 810°C/15 h + 810°C/10 h.

Fig. 3 shows XRD spectra of samples 3, 4 and 5 for which the sintering is at a temperature nearly the same, but during a time of 15, 60 and 72 h, respectively. After a sintering of 60 h, peaks corresponding to the 2201 phase appear. These peaks have been detected for $2\theta = 21.6°$, $25.2°$, $29.8°$ in Fig. 3c. On the other hand, the increasing of the peaks corresponding to (0 0 8), (0 0 10) and (0 0 12) plans reveal a more important texturation. No peak of the 2201 phase is detected in the Fig. 3b. Then, during a sintering, the 2201 phase begins to form from 15 to 60 h and is completely eliminated after 72 h.

3.2. SEM

Sample 1 has been photographed with two directions of the incident primary electron beam: perpendicular (Fig. 4a) and parallel (Fig. 4b) to the face of the sample. In the first photograph the size of the grains varies between 10 and 15 μm and have a flat shape. The second photograph shows a random orientation of the grains and an appreciable porosity.

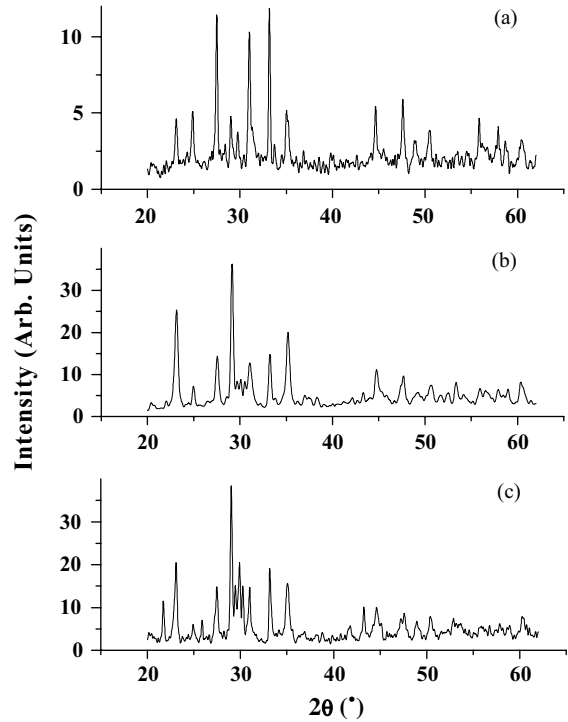The photograph of sample 2 (Fig. 4c) shows grains with flat shape and 2–7 μm size. The growth

Fig. 3. XRD Spectrum of the pellets (stoichiometric composition) sintered at: (a) 810°C during 15 h; (b) 820°C during 72 h; and (c) 820°C during 60 h.

of the grains is in form of layers parallel to the surface of the sample which is characteristic of the bismuth cuprates [2,13]. Narrow tubular shapes connect the grains.

In the SEM photograph of sample 3 (Fig. 4d) some grains have flat shape and a size of 5 μm. Some other grains have a longer shape as whiskers [14]. The grains are randomly distributed. The porosity of the sample is important.

3.3. Resistivity

The resistivity $\rho(T)$ of sample 1 is shown in Fig. 5. The onset of the superconducting transition T_c^{on} is at 90.6 K. The limit of the apparatus does not allow reaching the zero of resistivity which is under 77 K. The transition width is large. Many factors can explain this fact as porosity and volatility of Bi during sintering [15], confirmed by Tarascon et al. [16] with thermogravimetric measurements.
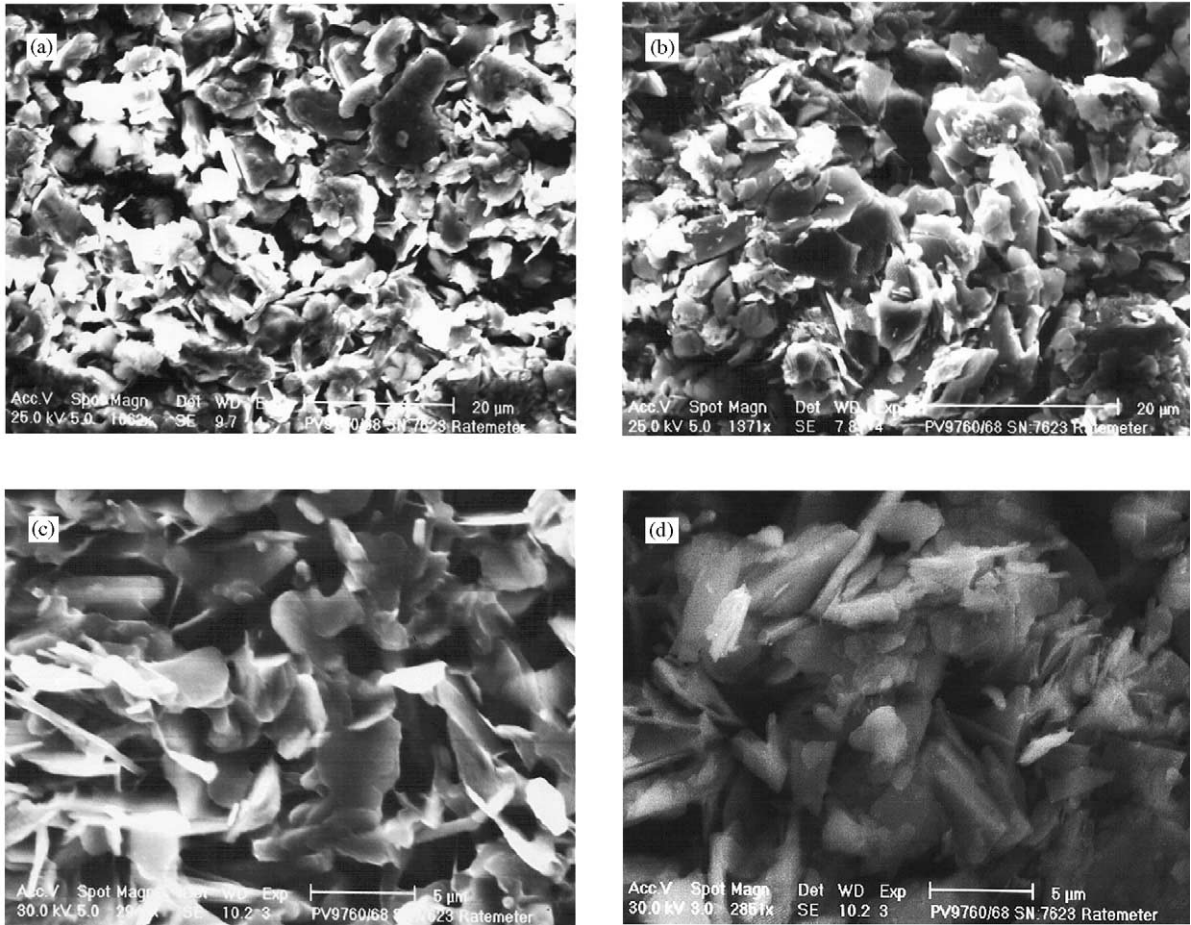
Fig. 4. SEM photographs of sample 1 (a), sample 1 (b) with an incident electron beam parallel, sample 2 (c) and sample 3 (d).

Sample 2 presents a lower T_c^{on} at 87.4 K (Fig. 5). Some fluctuations can be seen in the metallic portion of the plot. Bad intergrain connections and porosity, shown by the SEM photograph of Fig. 4a, can explain these fluctuations.

Fig. 6 shows the resistivities $\rho(T)$ of samples 3–5. After sintering during 25 h, sample 3 presents a semi-conducting behavior before the superconducting transition at 91.1 K (Fig. 6). The occurrence of 2201 phase explains this behavior. With a longer time of sintering of 60 h the 2201 phase is always present. The T_c^{on} is at 87.7 K. After a longer time of sintering, the metallic portion of $\rho(T)$ of sample 5 (Fig. 6) is more regular and the T_c^{on} is at
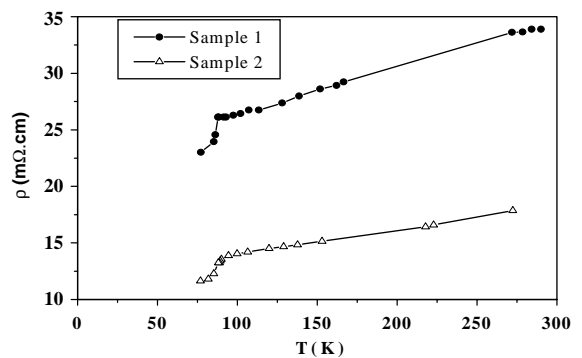

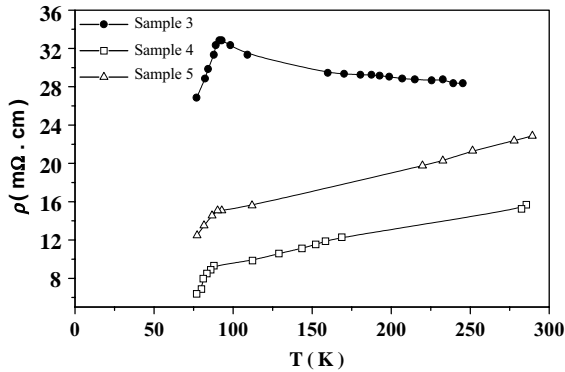Fig. 5. Resistivity $\rho(T)$ of samples 1 and 2.

Fig. 6. Resistivities $\rho(T)$ of samples 3–5.

90.7 K upper than the precedent onset temperature. Thus, we can say that the prolonged time of sintering improves the quality and the transport properties of the sample.

4. Conclusion

The conditions of elaboration have an influence on the transport properties of the sample obtained. We have shown that the pure Bi-2212 phase is obtained whether or not the starting composition is stoichiometric. With a non-stoichiometric composition the time of sintering is relatively low. The transition width is large. When the proportion of the starting compounds is stoichiometric the time of sintering is important. With the time of sintering, the sample goes from a semi-conducting

to a metallic behavior in its normal state of conduction. The prolonged time of sintering increases the onset temperature (T_c^{on}) and improves the conduction in the normal state and the quality of the sample.

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