ELABORATION AND CHARACTERIZATION OF SUPERCONDUCTING CERAMICS Bi$_2$Sr$_2$CaCu$_2$O$_{8+d}$

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Abstract

Samples of superconducting ceramics of Bi$_2$Sr$_2$CaCu$_2$O$_{8+d}$ have been elaborated starting from a mixture of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO. Different ways of initial firing have been tested for samples with different starting composition. X Ray Diffraction Powder (XRD) and Scanning Electron Microscopy show that, depending from starting composition and initial way of firing, some final samples present a pure superconducting phase.

Keywords: Bi-Sr-Ca-Cu-O system; Bi-2212, HTSC; Bismuth Cuprates.

1. Introduction

The bismuth based superconducting cuprates may exist in three different phases 2201, 2212 and 2223 characterized by the number of CuO$_2$ plans present in the crystallographic cell [1]. The solid state reaction is the most used and easy way to synthesize the superconducting phase Bi$_2$Sr$_2$CaCu$_2$O$_{8+d}$. The Bi-2212 phase is stable from 800°C to 850°C [2] when at higher temperatures the Bi-2223 phase is most stable (Fig. 1). The Bi-2212 superconducting ceramic is obtained by a process of several thermal treatments, as firing, sintering and sometimes annealing in oxygen atmosphere, of a mixture of carbonate and oxide powders. The different reactivities of the starting powders result in unavoidable forming of intermediary phases during Bi-2212 elaboration [3]. Bi$_2$Sr$_2$CaCu$_2$O$_{8+d}$ is a superconductor when d \(\leq 0.2\) [4]. There is not a great improvement of the superconducting properties of Bi-2212 induced by annealing under oxygen atmosphere as it is the case for YbaCuO [5]. In our work we study the influence of the conditions of the firing and successive thermal treatments on the final quality of the samples obtained.

\[
\begin{align*}
\text{Bi}_2\text{Sr}_2\text{O}_x & \\
\text{Bi}_2\text{Sr}_2\text{CaO}_x & \\
\text{Bi}_2\text{Sr}_2\text{CuO}_x & \\
\text{CaO} & \\
\text{Ca}_2\text{CuO}_3 & \\
\text{CuO} & 
\end{align*}
\]

\[T = 800^\circ\text{C}\]

Figure 1: Quasi-ternary diagram showing the Bi-2212 phase occurrence over 800°C.

2. Experiment

Following the solid state routine, Bi-2212 samples are usually elaborated starting from Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO mixed with a weight ratio Bi/Sr/Ca/Cu = 2/2/1/2. After a grinding in an agate mortar, the obtained powders were therefore fired in air at temperatures between 810°C and 835°C during 10 to 15 hours. With an
equilibrated ratio of the different elements in the starting mixture and after a calcination at 835°C during 15 hours, the phase Bi₂Sr₂.5Ca₀.5Cu₃Oₓ is obtained as it was revealed by XRD spectra compared to ASTM data base [6]. Moisture of the starting element powders can result in lack of stoichiometry of the elaborated compound [7]. Therefore, the CaCO₃ weight has been lightly increased when the SrCO₃ and CuO weights have been lightly lowered. Then the formula of the compound found to give the final stoichiometric Bi-2212 is Bi₂Sr₁.₆Ca₂₀.₆Cu₁.₃₃Oₓ. The fired mixture was ground again and pressed in pellet shape with a diameter of 13 mm and a thickness of 2 to 3 mm under an isostatic pressure of 2 Tons/cm². The obtained pellets were then sintered. Table I presents the conditions of firing and sintering of the different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Firing</th>
<th>Sintering</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>810°C / 15h</td>
<td>800°C / 10h</td>
</tr>
<tr>
<td>2</td>
<td>820°C / 15h</td>
<td>840°C / 15h</td>
</tr>
<tr>
<td>3</td>
<td>835°C / 10h</td>
<td>835°C / 10h</td>
</tr>
</tbody>
</table>

**Table 1**: Firing and sintering conditions of the samples.

After each step of the elaboration, the samples have been analyzed by XRD with a Siemens D8-Advanced powder diffractometer using a Bragg-Brentano geometry and copper Kα radiation (λCuKα=1.54060Å). Diffraction spectra peaks were identified using ASTM data base [6]. Without preparation, samples have been photographed using a Scanning Electron Microscope (SEM) Philips XL 30.

### 3. Results and discussion

#### 3.1. XRD analysis

Fig. 2 shows the XRD spectra of the calcinated powders and the sintered pellets. Bi-2212 phase is dominant in sample 1 calcinated (Fig. 2a). The diffraction peak corresponding to 2θ = 25.2° shows the weak presence of SrCO₃. In sample 2 the Bi-2212 phase is always dominant with increased intensity of the diffraction peaks (Fig. 2b). In the same figure, weak diffraction peaks of the parasitic phases CuO, SrCO₃, CaCO₃ and Ca₂CuO₃ may form during elaboration of Bi-2212 [8] or after substitution by samarium in the Bi-2212 phase [9]. The Bi-2212 phase is always dominant in sample 3 calcinated (Fig. 2c) with weak presence of SrCO₃, CaCO₃ and CuO. The presence of Ca₂CuO₃ is not detected in this sample. As it is characteristic in Bi-cuprates, satellite peaks can be observed for 2θ = 29.8°C in figures 2b and 2c. These satellite peaks show the existence of a modulated structure resulting from shifting of Bi and Sr atoms in a and c directions and Cu atoms in c direction [10]. Figs. 2d, 2e and 2f show the diffraction spectra of the three sintered samples. Diffraction peak intensities are remarkably more important after sintering which may be associated to a better texture or an increasing of crystallite volumes. Diffraction peaks corresponding to (00l) reflections are dominant in spectra of Figs. 2d and 2f, which means a preferential orientation parallel to ab plans. The diffraction peaks corresponding to (00l) plans and those corresponding to (11l) plans (Fig. 2e) have the same importance revealing absence of texture in sample 2 sintered. After sintering no detectable parasitic phase is found in the three samples.

#### 3.2. SEM analysis

The SEM photography of sample 1 is shown in Fig. 3. The sample presents grains of about 5 µm and someone reaching 10 µm. The small sintering time can explain the lightly high porosity of the sample revealed in Fig. 3. Some crystallites show the characteristic layered structure of Bi-cuprates. The photography shows that Bi-2212 grains are mainly randomly orientated. The very anisotropic structure of Bi-cuprates results on rapid initial growing [11]. After limited the initial growing, the grains impinged each other and stop growing. Additional heat treatments are needed to improve the macrostructural quality of the samples.
Figure 2: XRD spectra of: (a) calcined sample 1, (b) calcined sample 2, (c) calcined sample 3, (d) sample 1 sintered, (e) sample 2 sintered, (f) sample 3 sintered.

Figure 3: SEM photography of sample 1.
4. Conclusion

With only two steps, pure phases of superconducting ceramics Bi-2212 have been obtained, starting from powder of not very high purity. Bi$_2$Sr$_{1.9}$Ca$_{2.02}$Cu$_{1.33}$O$_x$ has been found to give final Bi-2212 stoichiometric. Weak presence of SrCO$_3$, CaCO$_3$, CuO and Ca$_2$CuO$_3$ is detected after calcination. XRD analysis confirms the purity of the Bi-2212 phases obtained. A texture is revealed for two samples. SEM photography shows a high porosity and some grains with characteristic layered structure of Bi-cuprates.

References