MM&FGM2014
São Paulo, Brazil Oct.19-22 2014

Spark plasma sintering of $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$: improving microstructural features for practical applications

I. García-Fornaris[1,2], I. Calzada[1], E. Govea-Alcaide[1], I. F. Machado[2], R. F. Jardim[3]

[1] *Facultad de Ciencias Técnicas, Universidad de Granma, Apdo. 21, P. O. Box. 85100, Bayamo, Cuba*
[2] *Escola Politécnica, Universidade de São Paulo, 05508-900, São Paulo, SP, Brazil*
[3] *Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo, SP, Brazil*

Abstract

The grain boundaries in polycrytalline high-T_c superconductors constitute a limitation for the use of these materials in several devices. In order to verify the effect of the consolidation process in the microstructural features, powders of single-phase $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) were consolidate by the spark plasma sintering (SPS) method at 750 °C. The SPS samples exhibited very high density but are oxygen deficient, as inferred from the electrical resistivity, $\rho(T)$, data. The samples were then subjected to a post-annealing heat treatment in air, at 750 °C, and for different times, $t_{pa} = 0$, 5, 30 min, and 40 hours. From the X-ray diffraction analysis we have found that SPS post-annealed samples for $t_{pa} > 5$ min show the presence of an extra phase identified as the infinite layer compound with general formula $Ca_{1-x}Sr_xCuO_2$. Irrespective of the presence of this additional phase, the superconducting properties, including the superconducting critical current at 77 K, of the post-annealed SPS samples are optimized for $t_{pa} = 5$ min. The combined properties of the samples obtained by the SPS technique make them suitable for practical applications as superconducting fault current limiters (SFCL).

Keywords: Bi-based Superconductor, Spark Plasma Sintering, Infinite Layer

1. Introduction

It is well known that an important issue in the fabrication of high-performance $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) and other superconducting cuprates is the improvement of their intergranular media. Samples with high density and homogeneous microstructure can be achieved only when both composition and grain growth can be controlled. The Spark Plasma Sintering (SPS) method, characterized by short sintering times and high heating rates, make it an useful tool for attaining this goal [1, 2]. The spark produced between grains may partially melt the grain boundaries, which combined with the compacting pressure applied simultaneously in a vacuum atmosphere lead to the production of samples with high density. However, the eventual melting of the intergranular media may be responsible for the suppression of superconductivity and the emergence of extra phases. The partial melting, combined with the low oxygen partial pressure and the rapid cooling introduce a delicate balance among variables which also involves grain with shell-core morphology, as discussed elsewhere [3, 4]. Thus, samples of cuprates prepared by the SPS technique usually have poor superconducting properties whose may be recovered by a post annealing heat treatment [3, 4]. Within this context, important details regarding changes caused by the post-annealing process performed on Bi-2223 prepared by the SPS method have not been sufficiently studied.

We present here our experimental results on samples of $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) processed by the SPS method. The samples were consolidated at 750 °C and under a pressure of 50 MPa. Emphasis was done on the role played by the post-annealing process in which samples were heat treated in air at 750 °C for different time intervals. We have observed that post-annealing heat treatment performed in a brief time interval is responsible for a partial reestablishment of the superconducting properties of the SPS samples. On the other hand, prolonged post-annealing treatments result in the formation of extra phases, as the infinite layer compound $Ca_{1-x}Sr_xCuO_2$ [5, 6].

Presenting author: I. F. Machado, machadoi@usp.br
Corresponding author: I. F. Machado, machadoi@usp.br

2. Experimental Procedure

Polycrystalline samples of $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$(Bi-2223) were prepared from powders of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO, which were mixed in an atomic ratio of Pb:Bi:Sr:Ca:Cu (0.35:1.65:2:2:3). The mixture was first calcined in air at 750 °C for 40 h, ground, and pressed into pellets of 15 mm in diameter and 2 mm in thickness at a pressure of 250 MPa. These pellets were heat treated at 800 °C in air for 40 h. Subsequently, the pellets were reground, pressed again, and sintered in air at 845 °C for 40 h. The last step was repeated three times. After the last heat treatment, the pellets were reground again and the resulting powder was used to be consolidated by the spark plasma sintering method. The above procedure assures that the obtained Bi-2223 precursor powder consists of the high-T_c Bi-2223 phase, as discussed elsewhere [7].

The final consolidation of the Bi-2223 precursor powder was performed in a SPS 1050 Dr Sinter$^®$ apparatus manufactured by Sumitomo Coal Mining Co. Ltd., Japan. During the sintering, the samples were heated from room temperature to $T = 750$ °C in 5 min, maintained at 750 °C for 5 min, and cooled within the sintering chamber. The entire sintering process was performed under vacuum ($\sim$10 Pa). The maximal compacting pressure used was 50 MPa, reached by a progressive increasing under the first 3 min of the SPS process. Then, the pressure remained at that value for 7 min. After this time, just when the sample begins to cooling down, the pressure is abruptly released [4].

The SPS samples have typical dimensions of 14.0 mm in diameter and $\sim$1.5 mm of thickness. The pristine SPS sample is referred as **SP-0** and others, which were subjected to a post-annealing heat treatment in air at 750 °C for different times: $t_{pa} = 5$ min (**SP-5**), 30 min (**SP-30**), and 40 hours (**SP-40**). The same Bi-2223 precursor powder was pressed into pellets at 50 MPa and sintered at 845 °C for 40 h in air (See Table 1). This sample is referred as the *reference sample*.

The density of the samples was measured by the Archimedes method. The crystal phase identification was evaluated from X-rays diffraction patterns obtained in a Bruker-XRD2 D8 Discover diffractometer. These measurements were performed at room temperature using Cu Kα radiation in the $3° \leq 2\theta \leq 80°$ range with a 0.05° (2θ) step size, and 5 s counting time. The standard dc four-probe method was used in all measurements of the electronic transport properties of the pellets [7], i.e. the electrical resistivity as a function of temperature, $\rho(T)$, and the critical current density measured at $T = 77$ K and at zero applied magnetic field, $J_c(0)$.

3. Results and Discussion

We start our discussion by noting that the **SP-0** sample, sintered by the SPS method, has a very high density ($\sim$ 5.7 g/cm^3), corresponding to nearly 90% of the theoretical density, a value much higher than $\sim$ 3.4 g/cm^3 of the *reference sample*. This confirms previous results and points out a drastic decrease of the porosity in the SPS samples [4]. Fig. 1 displays the X-ray diffraction patterns (XRD) taken in powders (left panel) and bulk samples (center and right panel). A careful inspection of Fig. 1 (a) (left panel) indicates that the procedure used for obtaining the Bi-2223 precursor powders resulted in single-phase materials and all indexed reflections are related to the high-Tc Bi-2223 phase. The XRD patterns of the other samples (*reference sample*, **SP-0**, and **SP-5**) also display single phase materials, further indicating that the SPS process results not only in very dense materials but it also preserves the single-phase nature of the powders. From the results of Fig. 1 (central panel) taken in pellets samples, one can observed extra peaks (market by IL) that increases with increasing post-annealing time, a feature which is much more evident in the post-annealed samples **SP-5**, **SP-30**, and **SP-40**. We have identified these extra peaks as belonging to a phase known as infinite layer (IL) with general formula $Ca_{1-x}Sr_xCuO_2$ [5, 6].

A possible explanation for the occurrence of the infinite layer phase involves not only the partial melting during the SPS consolidation but also important parameters of the method: the low partial oxygen pressure and/or the uniaxial compacting pressure used during the sintering process. The partial melting originates a rich calcium, strontium, and copper amorphous phase along grain boundaries. Due to the very high pressure used in the SPS process along with the post-annealing heat treatment in air at 750 °C, such an amorphous phase evolves to the infinite layer compound $Ca_{1-x}Sr_xCuO_2$. We also mention that the final stoichiometry of the infinite layer compound found in our SPS samples is still object of study, as previously discussed in the literature [8]. However, the huge increase of the intensity of the Bragg peaks belonging to the infinite layer compound with increasing post-annealing time, as observed in Fig. 1 (right panel), indicate that the temperature of the heat treatment promote the crystallization of underlaying infinite layer compound formed during the SPS consolidation. However, the above results need further investigation.
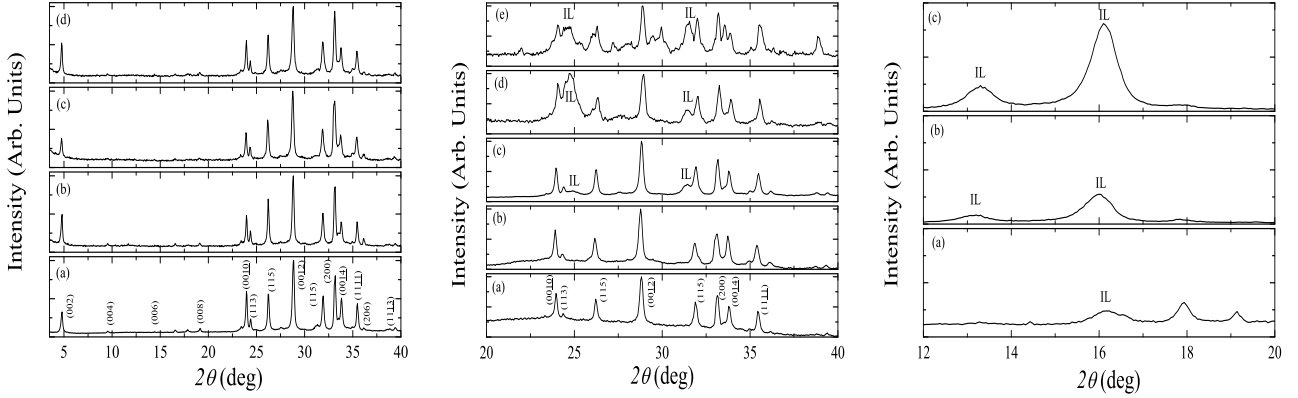
Figure 1: (left panel) XRD patterns of powders of (a) the Bi-2223 precursor, (b) *reference sample*, (c) **SP-0**, and (d) **SP-5**. (center panel) XRD of pellet samples of (a) *reference sample*, (b) **SP-0**, (c) **SP-5**, (d) **SP-30**, and (e) **SP-40**. (right panel) Expanded view of the XRD patterns of the post-annealed pellet samples for different post-annealing times $t_a = 5$ min (a), 30 min (b), and 40 hours (c). The relative intensity of the Bragg peaks belonging to the infinite-layer phase increases with increasing annealing time (right panel).

The temperature dependence of the electrical resistivity $\rho(T)$ of the studied samples is shown in Fig. 2 (a). Except for the **SP-0** sample, the other four samples display a metallic-like behavior in $\rho(T)$. The semiconducting-like behavior of the **SP-0** sample, displayed in the inset of Fig. 2, is compelling evidence of the occurrence of grains with shell-core morphology and indicates that the Bi-2223 samples, obtained by the SPS technique, are oxygen deficient. The metallic-like behavior seen in all post-annealed samples, similar to the *reference sample*, also suggests that the oxygen content in these SPS specimens play a very important role regarding their superconducting properties. Some of the parameters extracted from the $\rho(T)$ data are displayed in Table 1 and are of interest. We first mention here the onset superconducting critical temperature, T_{on} which is the highest for the **SP-40** sample. However, its superconducting transition width (T_{on} - T_{off}) assumes the highest value of the series, indicating that not only the oxygen content but also the volume fraction of the infinite layer compound, close related to the electrical resistivity at $T = 300$ K, $\rho(300$ K$)$, are important variables for producing high quality materials. However, the $\rho(T)$ displayed in Fig. 2 (a), combined with the parameters of Table 1, the $M(T)$ data (not shown), and XRD patterns, indicate that SPS samples are optimized when are prepared through the SPS method and post-annealed for 5 min in air at 750 °C.

An important feature of superconducting cuprates for practical applications is its superconducting critical current density, J_c, at 77 K. We have determined J_c at 77 K for all samples and the results are displayed in Table 1. Our results indicate that the *reference sample* has $J_c \sim 24$ A/cm^2 and that J_c increases appreciably in the post-annealed samples reaching values as high as ~ 82 and 44 A/cm^2 in samples **SP-5** and **SP-30**, respectively. A further increase in t_{pa} up to 40 h showed to be deleterious to the material, certainly due to the presence of the infinite layer phase, and J_c was only ~ 14 A/cm^2.

We have also studied the magnetic field dependence of critical current density, $J_c(B_a)/J_c(0)$ measured at $T = 77$ K, as displayed in figure 2 (b). The data clear show two different behaviors. The first one, referred as Josephson-like behavior, in which $J_c(B_a)/J_c(0)$ decreases fast with increasing B_a, is seen in **SP-40** and in the *reference sample*

Table 1: Extracted parameters from transport measurements performed in all samples studied: the onset superconducting critical temperature, T_{on}; the offset superconducting critical temperature, T_{off}; the electrical resistivity at $T = 300$ K, $\rho(300$ K$)$, and the critical current density at zero applied magnetic field and at $T = 77$ K, $J_c(0)$.

Sample	T_{on} (K)	T_{off} (K)	$\rho(300$ K$)$ (mΩcm)	$J_c(0)$ (A/cm^2)
reference sample	106.4	102.3	8.1	23.7
SP-0	89.1	68.7	22.7	-[a]
SP-5	104.6	101.1	4.2	82.5
SP-30	111.7	104.5	3.6	43.5
SP-40	115.5	94.1	4.4	14.1

[a]Notice that the sample **SP-0** attains the superconducting state at $T_{off} \sim 69$ K, that is less than the measuring temperature of $J_c(0)$ (see Section 2).
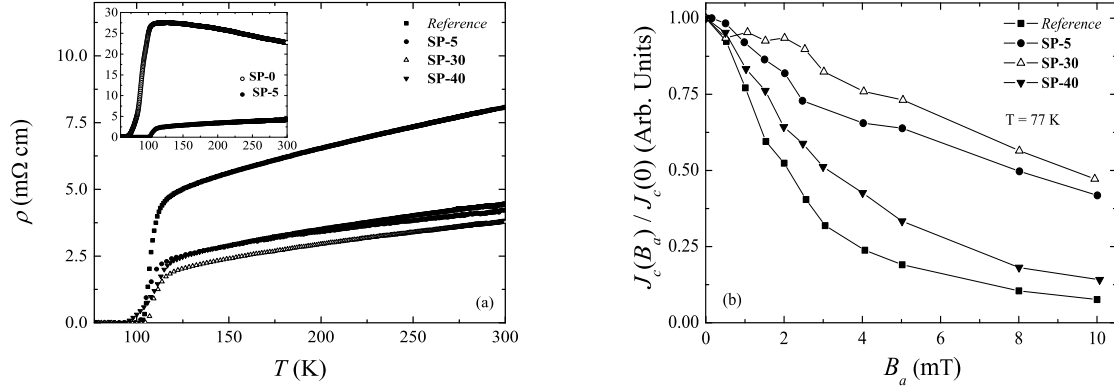
Figure 2: (a) Temperature dependence of the electrical resistivity, $\rho(T)$, of all studied samples. The inset displays the $\rho(T)$ dependence of two SPS samples: **SP-0** and **SP-5**. (b) Magnetic field dependence of the critical current density, $J_c(B_a)/J_c(0)$, at $T = 77$ K of the annealed SPS samples.

[10]. The clear Josephson-like behavior observed here suggests that the materials are comprised of grain boundaries with very high values of electrical resistance, that limits the grains connectivity, and therefore decreases the ratio $J_c(B_a)/J_c(0)$ even in very small B_a. A quite different behavior has been observed in samples **SP-5** and **SP-30**, where $J_c(B_a)/J_c(0)$ is much less B_a dependent. This indicates that the post-annealing process, besides raising the superconducting critical temperature of the grains and the superconducting volume fraction (not shown) has produced appreciable changes in the grain boundaries of these samples.

4. Conclusions

Our experimental results point out that samples produced by the SPS technique are dense, have grains with a core-shell morphology, where the shell is oxygen deficient, and deserve a post-annealing heat treatment for restoring the superconducting properties of the starting material. These results strongly suggest that the use of a non-reducing die, instead a graphite die, can minimize the deoxygenation of the samples during SPS process. We have also found that there is a delicate balance between oxygen-deficiency and the occurrence of an extra phase at the intragranular medium. The post-annealing heat treatment, performed in air, at 750 °C and for different time intervals, alters significantly several properties of the samples. However, the combined results of structural, magnetic, and transport properties indicate that the superconducting properties of SPS Bi-2223 samples are optimized when are post-annealed for 5 min. It is worth mentioning that the high density obtained in the SPS samples combined with transport and magnetic properties point out for building devices as superconducting fault current limiters (SFCL).

References

1. V. Mamedov, Powder Metallurgy **45** (2002) 322.
2. E. A. Olevsky, S. Kandukuri, L. Froyen, J. Appl. Phys. **102** (2007) 114913.
3. S. Zhang, C. Li, Q. Hao, P. Zhang, H. Liu, S. Yang, Physics Procedia **27** (2012) 176.
4. E. Govea-Alcaide, I. F. Machado, M. Bertolete-Carneiro, P. Muné, R. F. Jardim, J. Appl. Phys. **112** (2012) 113906.
5. E. M. McCarron, M. A. Subramanian, J. C. Calabrese, R. L. Harlow, Mat. Res. Bull. **23** (1988) 1355.
6. H. Shaked, Y. Shimakawa, B. A. Hunter, R. L. Hitterman, J. D. Jorgensen, P. D. Han, D. A. Payne, Phys. Rev. B **51** (1995) 11784.
7. P. Muné, E. Govea-Alcaide, R. F. Jardim, Physica C **384** (2003) 491.
8. J. L. MacManus-Driscoll, P. Wang, J. C. Bravman, R. B. Beyers, Appl. Phys. Lett. **65** (1994) 2872.
9. T. Fujii, T. Watanabe, A. Matsuda, Physica C **357** (2001) 173.
10. E. Govea-Alcaide, I. Garcia-Fornaris, P. Mune, R. F. Jardim, Eur. Phys. J. B **58** (2007) 373.