Spark plasma sintering consolidation of Bi$_{1.65}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ ceramic samples

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Abstract. Pre-reacted powders of (Bi-Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ (Bi-2223) were consolidated by using the spark plasma sintering (SPS) technique under vacuum and at different consolidated temperatures $T_D$. We have found that the transport properties of SPS samples depend on their oxygen content because the SPS process is performed under vacuum. From these results we have inferred that SPS samples are oxygen deficient and that a post-annealing treatment, performed in air for a brief time interval, is needed to restore such a deficiency. Measurements of temperature dependence of the thermal conductivity, $\kappa(T)$, were performed in all SPS samples including a reference sample sintered at 845 $^\circ$C in air. The results indicate that the electronic contribution to the thermal conductivity in all samples is very low. Values of $\kappa$ were found to be higher in SPS samples mostly because of their high volume density of $\sim$ 5.7 g/cm$^3$. We have also performed measurements of the critical current density as a function of the applied magnetic field, $J_c(B_a)$. All samples display a clear Josephson-like behavior and low values of the superconducting critical current density at zero applied magnetic field. The experimental results indicate that the oxygen deficiency in SPS samples is marked near the grain boundaries. This suggests the occurrence of grains with core-shell morphology, where the width of the shell is consolidation temperature dependent.

1. Introduction
The spark plasma sintering (SPS) is an effective, unconventional method that promotes densification by the simultaneous action of a high direct electric current through graphite dies and uniaxial pressure [1]. In high-$T_c$ cuprates superconductors, the use of SPS can be a difficult task because the process occurs under vacuum, and these materials are very sensitive to the oxygen content. Such an obstacle is less noticeable in compounds of the Bi-Sr-Ca-Cu-O (BSCCO) system [2], making them excellent candidates for the application of the SPS technique. However, up to now there are few studies regarding the use of SPS in the BSCCO system. In the last decade, the influence of the SPS conditions on the formation of (Bi,Pb)$_2$Sr$_2$Ca$\delta$Cu$_2$O$_{8+\delta}$ (Bi-2212) and (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_2$O$_{10+\delta}$ (Bi-2223) phases was conducted [3]. In this study, the materials were SPS under different holding temperatures and times, and the uniaxial compacting
pressure was only 17.5 MPa. Under these conditions, the consolidated samples exhibited extra, non-superconducting phases. In addition to this, the SPS samples showed semiconducting-like behavior in the normal state region, broad superconducting transitions, and very low values of the superconducting transition temperature. The authors attributed the results to the presence of extra phases and their distribution within the samples.

Recently, we have reported a systematic study on the influence of the consolidation temperature $T_D$ on the normal and superconducting transport properties of Bi-2223 ceramics samples obtained by using the SPS technique [4]. Similar results as those mentioned in Ref. [3] were obtained. However, after the SPS, the dominant phase in all samples was the Bi-2223. In addition to this, the relative density of the pellets reached $\sim 85\%$ of the theoretical value by using an uniaxial compacting pressure of 50 MPa. We have found that the normal and the superconducting transport properties of the SPS samples were strongly dependent on their oxygen content because the process occurs under vacuum. Under these circumstances, a post-annealing treatment was needed to improve the transport properties of the samples [4].

In this paper, we report on the thermal and electrical properties of Bi$_{1.65}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ ceramic samples consolidated by the SPS technique at different temperatures. We have also studied the role of the post-annealing treatment for the improvement of the superconducting properties of the SPS samples.

2. Experimental procedure
Polycrystalline samples of Bi$_{1.65}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ (Bi-2223) were prepared by the traditional solid state reaction method as described elsewhere [5]. The final consolidation of the samples was performed in a SPS 1050 Dr Sinter apparatus [4]. In order to study the influence of the consolidation temperature, $T_D$, the samples were subjected to two different temperatures $T_D = 750$ and $830 \, ^\circ C$. The maximum uniaxial compacting pressure used in these experiments was 50 MPa. Also, the SPS samples were subjected to an additional post-annealing heat treatment in air at 750 $^\circ C$ during 5 minutes [4]. Additionally, for comparison reasons, $\sim 4$ g of the starting powder was cold pressed inside the SPS apparatus and the resulting pellet was sintered at 845 $^\circ C$ in air for 2400 min. This sample (84PA) will thereafter be referred as the reference sample.

The temperature dependence of the electrical resistivity, $\rho(T)$, and transport critical current density as a function of the applied magnetic field, $J_c(B_a)$, were performed by using the procedures reported elsewhere [4, 5]. The thermal conductivity measurements were carried out on parallelepiped-shaped samples with approximate dimensions of $5 \times 1.5 \times 1 \, mm^3$ in the temperature range of 2 - 300 K using the thermal transport option (TTO) of the Quantum Design PPMS system [6].

3. Results and discussion
Our previous results indicated that the SPS method significantly promotes the densification of the pre-reacted powders and produces nearly single phase (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ ceramic samples [4]. The density of the reference sample (84PA), uniaxially pressed at 50 MPa, was only $\sim 3.2 \, g/cm^3$, but increased to $\sim 5.7 \, g/cm^3$ in SPS samples consolidated at the same low compacting pressure. However, there are important points to be addressed here: the SPS samples are sintered under vacuum, at high temperatures, and in a short time interval [4]. These features affect the properties of the SPS samples, as discussed below.

The $\rho(T)$ data of the samples 83PA and 83PA75 are displayed in Fig. 1. Both samples were consolidated by SPS at $T_D = 830 \, ^\circ C$ and, in addition, the latter was post-annealed at 750 $^\circ C$ for 5 min in air. The sample 83PA exhibits a clear semiconductor-like behavior in which $\rho(T)$ increases with decreasing temperature, reaches a maximum at $T \sim 118 \, K$, which is followed by a very broad superconducting transition. In contrast, the $\rho(T)$ behavior of sample 83PA75 displays a typical metallic behavior and an abrupt resistive superconducting transition. These different features between samples were interpreted by considering that the
deoxygenation process in SPS samples preferably takes place near the grain-boundaries, leading to the occurrence of grains with core-shell morphology where the shell is oxygen deficient and that the width of shell increases with increasing $T_D$ [4].

Figure 2 displays the temperature dependence of the thermal conductivity, $\kappa(T)$, of the samples 84PA, 75PA, 75PA75, 83PA, and 83PA75. The total thermal conductivity consists of the lattice and the electronic (carrier) contribution, which is connected to the electrical conductivity, in first approximation, by the Wiedemann-Franz law. In all samples, $\kappa(T)$ increases with increasing temperature between 2 to 300 K and SPS samples were found to display higher ($\sim 2$ times) values of $\kappa(T)$ when compared with the reference sample. Such a feature is more pronounced in the normal-state region ($T \geq T_c^\ast$) and is certainly related to the higher volume density of SPS samples which displays a very low concentration of voids. We have also found that $\kappa(T)$ exhibits a linear behavior in the temperature range $220 \leq T \leq 300$ K (see Fig. 2). We attribute the deviation of such a linear behavior below $\sim 220$ K to the pseudogap formation, a feature corroborated by changes observed in the same $T$ window in $\rho(T)$ data, probably related to a decrease of the free carriers due to the pseudogap formation [7].

As a first attempt to estimate the electronic contribution to $\kappa(T)$, we have used the the Wiedemann-Franz law, $\kappa_e(T) = (L_0 T)/\rho(T)$, where $L_0 = 2.45 \times 10^{-8}$ WΩ/K² is the Lorentz number. Table 1 displays the estimated values of $\kappa_e$ contribution to the thermal conductivity for all samples at $T = 300$ K. We first point out that all values are at least one order of magnitude smaller than the measured $\kappa$ value at this temperature. This indicates that $\kappa(T)$ is mainly governed by the phonon contribution, as described elsewhere [8]. The results also suggest that the large phonon contribution to $\kappa(T)$ is present as well in post-annealed samples in which the electrical resistivity values are lower. Under these conditions, grain-boundaries seems to be a more plausible source of electron scattering for the decrease in $\kappa(T)$ and such a decrease is

Table 1. Some parameters of the samples studied in this work (see the text for details).

| Sample   | $T_{off}$ (K) | $\rho$(300K) (mΩ cm) | $\kappa_e$(300K) (K) | $T_c^\ast$ (K) | $J_c(0)$ (A/cm²) | $B_0$ (mT) |
|----------|---------------|-----------------------|----------------------|----------------|-----------------|-------------|
| 84PA     | 101.0         | 9.3                   | 0.08                 | 106            | 1.4             | 1.02        |
| 75PA     | 83.0          | 10.0                  | 0.07                 | 101            | 2.4             | 0.64        |
| 75PA75   | 102.6         | 4.3                   | 0.17                 | 108            | 6.5             | 1.44        |
| 83PA     | 81.0          | 32.6                  | 0.02                 | 99             | 1.3             | 0.42        |
| 83PA75   | 102.6         | 6.8                   | 0.11                 | 108            | 3.5             | 0.82        |
field B samples consolidated at 830 B are smaller than that measured in the reference sample 83PA, 75PA75, 83PA, and 83PA75. Here, the solid line is a visual guide to show the range where κ data have a linear behavior. (b) An expanded view of the κ(T) data in the 2 - 150 K range. T_c^\kappa is defined as the superconducting critical temperature. The lines are a guide for the eyes (see the text for details).

Figure 2. (a) Temperature dependence of the thermal conductivity of the reference sample 84PA and the SPS samples 75PA, 75PA75, 83PA, and 83PA75. Here, the solid line is a visual guide to show the range where κ data have a linear behavior. (b) An expanded view of the κ(T) data in the 2 - 150 K range. T_c^\kappa is defined as the superconducting critical temperature. The lines are a guide for the eyes (see the text for details).

Figure 3. Normalized J_c(B_a)/J_c(0) curves measured in samples 75PA and 75PA75 (a), and 83PA and 83PA75 (b). For comparison reasons the curve measured in the sample 84PA was included in both panels. Measurements were performed at the same reduced temperature t = T/T_0 = 0.94. Dashed lines are guide for the eyes and indicate the position of the critical field of the Josephson junctions (see text for further details).

much less market is all SPS samples with very high density.

The features occurring at the grain-boundaries have enormous influence on the behavior of J_c(B_a). Figure 3 displays the normalized J_c(B_a)/J_c(0) virgin curves measured in samples 84PA, 75PA, 75PA75, 83PA, and 83PA75. For comparison reasons, the above measurements were performed at the same reduced temperature, t = T/T_0 = 0.94, very close to the temperature in which the zero resistance state is observed (see Table 1) and the flux penetration is robust. Values of the critical current density at zero applied magnetic field, J_c(0), are reported in the Table 1. Due to the proximity to T_0, values of J_c(0) are very low in all samples, providing extra information regarding the relative change of the transport properties after the post-annealing treatment. The critical current density increases ~ 2.7 times in SPS samples obtained at the same consolidation temperature. On the other hand, as compared to the reference sample, J_c(0) was found to raise ~ 4.5 times (sample 75PA75) and only ~ 2.7 (sample 83PA75). All curves exhibit a clear Josephson-like behavior, in which the ratio J_c(B_a)/J_c(0) abruptly decreases with increasing B_a. We first mention here that values of J_c(B_a)/J_c(0) in the SPS samples 75PA and 83PA are smaller than that measured in the reference sample, further indicating the major role played by the oxygen content in the transport properties of the materials (see Table 1). We also mention that the decrease in J_c(B_a)/J_c(0), for the same B_a range, is much more pronounced in samples consolidated at 830 °C, indicating that the flux penetration through grain boundaries is significant in these samples.

In order to further address the flux penetration, a particular value of the applied magnetic field B_0, where J_c(B_a)/J_c(0) decreases ~ 50 %, is of interest [9]. Such a magnetic field is referred to as the critical field of the Josephson junctions, B_0 = \Phi_0/(2\lambda_L L_g). Here, \Phi_0 is the flux quantum, \lambda_L is the London penetration depth, and L_g is the grain size. The obtained values
of $B_0$ are listed in Table 1. Despite of the fact that values of $B_0$ are very small in all samples, a 2-fold increase after the post-annealing treatment is clearly observed. Previous results in Bi-2223 sample yielded a value of 1.5 mT at $T = 77$ K in a sample pelletized at 50 MPa and with volume density of $\sim 4.0$ g/cm$^3$ [5]. We mention here that a similar value was found in the 75PA75 sample but at $T = 96.4$ K.

By assuming that the SPS process unaffects significantly the size of the grains, values of $B_0$ between samples can be related to changes in the $\lambda_L$ of the materials. In this regard, increasing $B_0$ results in a decrease of $\lambda_L$. The observed behavior of $B_0$, and consequently of $\lambda_L$, can be implicitly related to changes in the width of the oxygen deficiency shell near the grain boundaries, as suggested previously [4]. A preliminary analysis suggests that $\lambda_L$ is larger in samples consolidated at higher temperatures, further indicating a thicker oxygen-deficient shell of these SPS samples.

4. Conclusions

We have used the spark plasma sintering (SPS) method to consolidated pre-reacted powders of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+y}$ (Bi-2223) compounds. All samples were uniaxially pressed at 50 MPa and the influence of the consolidation temperature on the physical properties was investigated and compared with a sample synthesized by the solid-state reaction method (reference sample). The SPS samples are oxygen deficient and are believed to be comprised of grains with a shell-core morphology. The electronic contribution to the thermal conductivity in all samples is very low. Values of $\kappa$ were found to be higher in SPS samples because of their high volume density ($\sim 5.7$ g/cm$^3$) as compared with the reference sample ($\sim 3.2$ g/cm$^3$). We have also observed a Josephson-like behavior of $J_c(B_a)$ and have obtained the critical field of the Josephson junctions, $B_0 \propto \lambda_L^{-1}$. A preliminary analysis indicate that increasing $B_0$ decreases $\lambda_L$ in the post-annealed samples and that result is related to changes in the width of the oxygen-deficient shell of the superconducting grains.

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