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ORIGINAL PAPER

Spark Plasma Sintering of $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ Superconducting Samples: Evaluation of Microstructure and Mechanical Properties

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Abstract Powders of single-phase $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) were consolidated by the spark plasma sintering (SPS) method at 750 °C. The SPS samples exhibited very high density, but are oxygen deficient, as inferred from magnetization, $M(T)$, data. Therefore, the samples were then subjected to a post-annealing heat treatment in air, at 750 °C for 5 min. From the combined data of X-ray diffraction, microstructures observed by SEM, and Vickers microhardness measurements, we have found that SPS post-annealed samples showed the presence of an extra phase. According to the EDS analysis and X-ray diffraction results, the extra was identified as an infinite layer compound with general formula $Ca_{1-x}Sr_xCuO_2$. Irrespective of the presence of this additional phase, the superconducting properties of post-annealed SPS samples are optimized when they are heat treated in air, at 750 °C for just 5 min. We have also observed a decrease in the Vickers as well as different indentation features in post-annelaed samples when compared with SPS ones. The occurrence of a decohesion of grains has been also observed, a feature similar to that found previously in the same material. On the other hand, a pile up formation occurred throughout the indentation in the sample, in which the annealing was carried out. 3-D profilometer characterizations confirmed these results, which are close related to the occurrence of the extra phase $Ca_{1-x}Sr_xCuO_2$.

Keywords Bi-based superconductor · Spark plasma sintering · Infinite layer

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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 may 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, is a useful tool for attaining this goal [1, 2].

In previous works [3, 4], pre-reacted powders of $(Bi\text{-}Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ were consolidated by using the SPS technique at different temperatures T_D = 750, 800, and 830 °C. The obtained results indicated indicated that the materials consist of the Bi-2223 dominant phase and some traces of $Bi_2Sr_2CaCu_2O_{10+x}$ (Bi-2212) were found in all samples. Also, the volume density of the SPS pellets reached ∼85 % of the theoretical value by using an

uniaxial compacting pressure of 50 MPa. It was found that only the sample consolidated at 750 °C (lower T_D) exhibits better superconducting and normal-state transport properties. It seems that 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 partial melting combined with the low oxygen partial pressure and the rapid cooling introduces a delicate balance between variables which also involves grains with shell-core morphology, where the shell is oxygen deficient [3, 5]. Thus, samples of cuprates prepared by the SPS technique usually have poor superconducting properties when compared with those prepared by the conventional method by using the pre-reacted powders. The experimental results also revealed that transport properties of SPS samples may be recovered when properly subjected to a post-annealing heat treatment [3–5]. Better results were achieved when the SPS sample consolidated at $T_D = 750$ °C was subjected to a post-annealing treatment in air at 750 °C for a brief time interval (5 min) [3].

Within this context, we describe here our experimental investigation performed on samples of Bi-2223 processed by the SPS method. The specimens were consolidated at 750 °C under a uniaxial pressure of 50 MPa. Notice that, as previously reported [3, 4], the above consolidation conditions produce better superconducting samples by spark-plasma sintering. Here, emphasis was done to the role played by the post-annealing process. We have observed that post-annealing heat treatments performed in a brief time interval, as fast as 5 min, is responsible for a partial reestablishment of the superconducting properties of the materials and may promote the formation of extra phases, as the infinite layer compound $Ca_{1-x}Sr_xCuO_2$ [6, 7]. This layered compound has been identified by X-ray diffraction analysis, and microstructural characterization using energy dispersive analysis (EDS) obtained by scanning electron microscopy (SEM). The results corroborate our previous findings [3, 4, 8, 9]. Vickers microhardness were also carried out and the features of the indentation were compared to other results found in the literature [10–12].

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 SPS method. The above procedure assures that the obtained Bi-2223 precursor powder consists of the high-Tc Bi-2223 phase, as discussed elsewhere [14].

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 SPS process is performed under vacuum (∼10 Pa). The maximal compacting pressure used was 50 MPa, reached by a progressive increase during the first 3 min of the SPS process and it remains fixed at this valued for about 7 min. After this time interval, just when the sample begins to cool down, the pressure is abruptly released [3]. The SPS samples have typical dimensions of 14.0 mm in diameter and 1.5 mm thickness. The pristine SPS sample is referred here as SP-0 and the sample which was subjected to a post-annealing heat treatment in air at 750 °C for 5 min is referred to as SP-5. The results of SPS samples were compared to the same Bi-2223 precursor powder that was pressed into pellets at 50 MPa and sintered at 845 °C for 40 h in air, designed *reference sample*, obtained in a previous work [3].

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 scanning electron microscopy (SEM) micrographs were taken with a JEOL JSM-6010LA Analytical Scanning Electron Microscope operated at 20 kV. Analysis of atomic sample composition has been made by means of energy dispersive X-ray spectroscopy (EDS).

Measurements of DC magnetization, $M(T)$, were performed in a commercial SQUID magnetometer from Quantum Design in powder samples under both zero-field-cooled (ZFC) and field-cooled (FC) conditions.

An attempt of the evaluation of the mechanical properties was carried out by Vickers Microhardness. Different loads were applied in the range of 100 to 2000 gf. The equipment used was a Buehler Microhardness tester (Micromet 2103). However, indentations were hard to observe by optical microscopy and they were evaluated by SEM. The indentation characterized was 2000 gf load. A profile of indentations was also obtained by a 3-D profilometer equipment (CCI MP-Taylor Hobson), which allowed to evaluate the indentation main features.

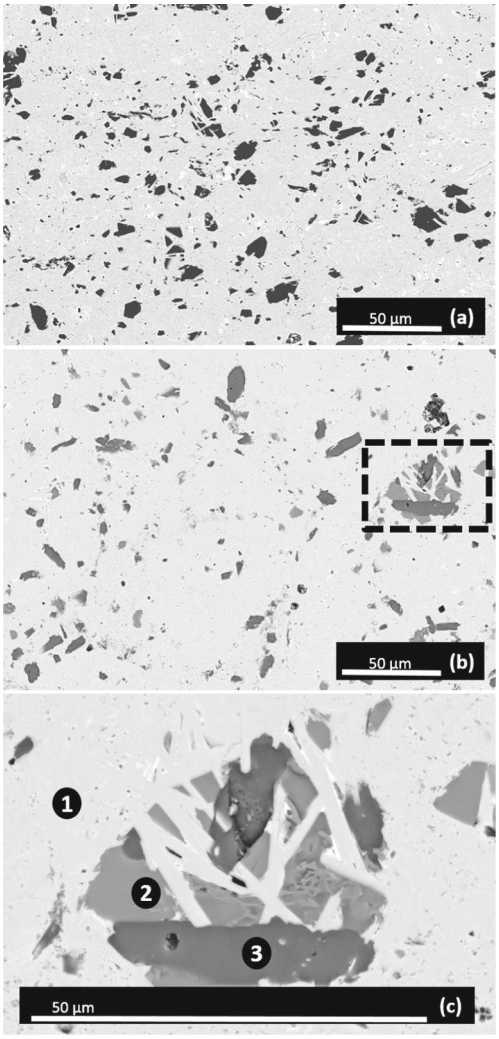

Fig. 1 SEM images (*back scattered electrons images*) **a** sample SP-0, **b** SP-5 sample, and **c** expanded view of SP-5 sample showing details of the microstructure in which crystal phases identified by different *gray shades* may be observed. The image correspond to the surface of the sample perpendicular to the applied pressure direction. The chemical compositions of points 2 and 3 were found to be very similar

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 (∼5.7 g/cm^3), corresponding to nearly 90 % of the theoretical density, a value much higher than 3.4 g/cm^3 of the *reference sample* [3]. This confirms previous results and points out a drastic decrease of the porosity in SPS samples [3].

We also mention that such a very high density is mirrored in the microstructures of samples SP-0 and SP-5, as displayed in Fig. 1. The images exhibit microstructures of dense materials, with low porosity, but with different features. The first important result here is that both samples are comprisied of a majority phase that coexists with another one, a feature much more pronounced in sample SP-5. To put this point in perspective, a detailed region of sample SP-5, as displayed in the Fig. 1b, must be considered. The back scattered electrons image of this particular region allowed the observation of shades of gray, further indicating different crystal phases. EDS analysis was then performed to verify the chemical composition of the phases observed. Table 1 displays the results of the EDS analysis in the regions where different gray shades are observed. Black regions are related to pores due to particle detachment during the metallographic sample preparation. This region is observed in Fig. 1c and has almost the same composition of the region indicated by 2, from Fig. 1c. Therefore, the brighter regions indicated by 1 in Fig. 1c are rich in Pb and Bi than the other ones, which was identified as Bi-2223 phase. On the other hand, the dark gray regions are very poor in Bi and Pb, but have higher contents of Cu and Sr (see Fig. 1c and EDS analysis results in Table 1). Therefore, there is a definite difference in the chemical composition between regions we have termed black dark gray and light gray. Another result to point out is the presence of carbon in our samples. It has been detected mainly in the dark gray regions, a feature accompanied by a very high content of oxygen. Therefore, the post-annealing heat treatment, and consequently the increase in the oxygen content of the samples, was responsible for changes in the microstructure of the specimens.

Figure 2 displays the X-ray diffraction patterns (XRD) performed in bulk samples. The Bragg peaks of the SP-0 sample (Fig. 2a) were all identified as belonging to the (Bi-2223) crystal phase, as described elsewhere [3, 14]. On the other hand, we have also observed the occurrence of extra peaks, identified as IL, in the post-annealed sample SP-5. These extra peaks were ascribed to a phase known as infinite layer (IL), with general chemical formula $Ca_{1-x}Sr_xCuO_2$ [15]. Therefore, the results from the X-ray diffraction data

Table 1 EDS spectra of the different regions identified on the sample **SP-5**

	Point 1		Point 2	
Elt.	mass %	atm. %	mass %	atm. %
Bi	40.06	14.81	1.59	0.30
Pb	11.38	4.24	–	–
Sr	16.87	14.88	20.73	9.32
Ca	6.05	11.66	8.45	8.31
Cu	19.21	23.36	49.84	30.89
O	6.43	31.05	15.18	37.36
C	–	–	4.22	13.83

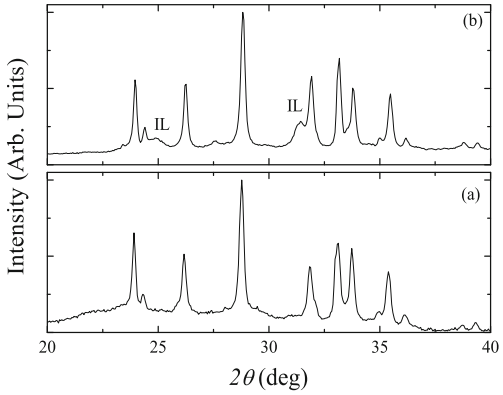

Fig. 2 XRD patterns of pellet samples of **a** SP-0, and **b** SP-5. The extra peaks belonging to the infinite-layer phase (marked as IL) appears after the post-annealing treatment

are in excellent agreement with the EDS results in which an extra phase, very poor in Bi and Pb, was found.

A possible explanation for the occurrence of the infinite layer phase involves not only the partial melting during the SPS consolidation process but also important parameters of the method: the low partial oxygen pressure and 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 compacting 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 [15].

The presence of extra phases in our samples may influence their magnetic properties, as one may see in the temperature dependence of magnetization data displayed in Fig. 3. The figure displays the zero-field cooling (ZFC) magnetization $M(T)$ curves measured in bulk samples under an applied magnetic field of B_a = 5 mT. Two features are of interest in the $M(T)$ data. First, the superconducting critical temperature of the grains, T_{cg}, is appreciably reduced to ∼101 K in the SP-0 sample while it is T_{cg} ∼108 K in post-annealed sample SP-5 (see inset of the figure). Such a result indicates that the SPS process, performed under a very low oxygen pressure, results in samples which are oxygen deficient. Such a deficiency in oxygen has a definite influence in the superconducting critical temperature of the grains T_{cg} which is expected to decrease with increasing oxygen deficiency, as discussed elsewhere [16]. This result is also important for supporting the shell-core morphology of the grains, previously suggested for SPS samples consolidated in low oxygen pressure environment, where an oxygen deficient shell surrounds the superconducting grains of the material [3, 4].

Another experimental result of interest is related with the magnitude of the $M(T)$ sign at 5 K, that reaches its minimum value for the SP-0 sample and increases appreciably for the other sample. The magnitude of the the $M(T)$ sign, transformed into Meissner (or superconducting) fraction ($4\pi\chi$), indicates that the post-annealing heat treatment introduce a delicate balance between the recovering of the oxygen concentration of the samples, the superconducting properties of the SPS specimens, and the formation of extra phases.

The results described above indicated that the superconducting cuprate $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi-2223) may be synthesized by the SPS process and that the the post-annealing heat treatment, important for the reestablishment of the superconducting properties, may alter the microstructures of the materials. Such changes and modifications may improve the electronic properties of the Bi-2223 material, by altering its oxygen content, but are also responsible for the occurrence of extra phases. The combined properties of the samples obtained by the SPS technique make them suitable for practical applications as, for instance, superconducting fault current limiters (SFCL). However, for this kind of practical application, the mechanical properties of the material may be evaluated. The evaluation of the mechanical properties of our SPS samples were carried out by Vickers microhardness tests. Different loads were applied, but nevertheless, it was not possible to measure the diagonals of the indentation by optical microscopy. Therefore, the SEM evaluation was conducted and the indentations of the SP-0 and SP-5 samples were performed and are displayed in Fig. 4.

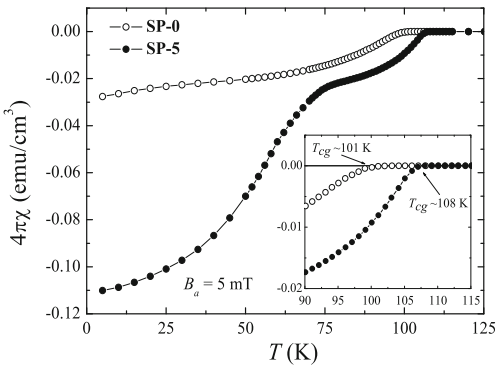

Fig. 3 Temperature dependence of magnetization measured in bulk samples under an applied magnetic field of 5 mT. Only the ZFC branches are displayed in the figure. Changes in T_{cg} are seen after the post-annealing heat treatment performed at 750 °C for 5 min

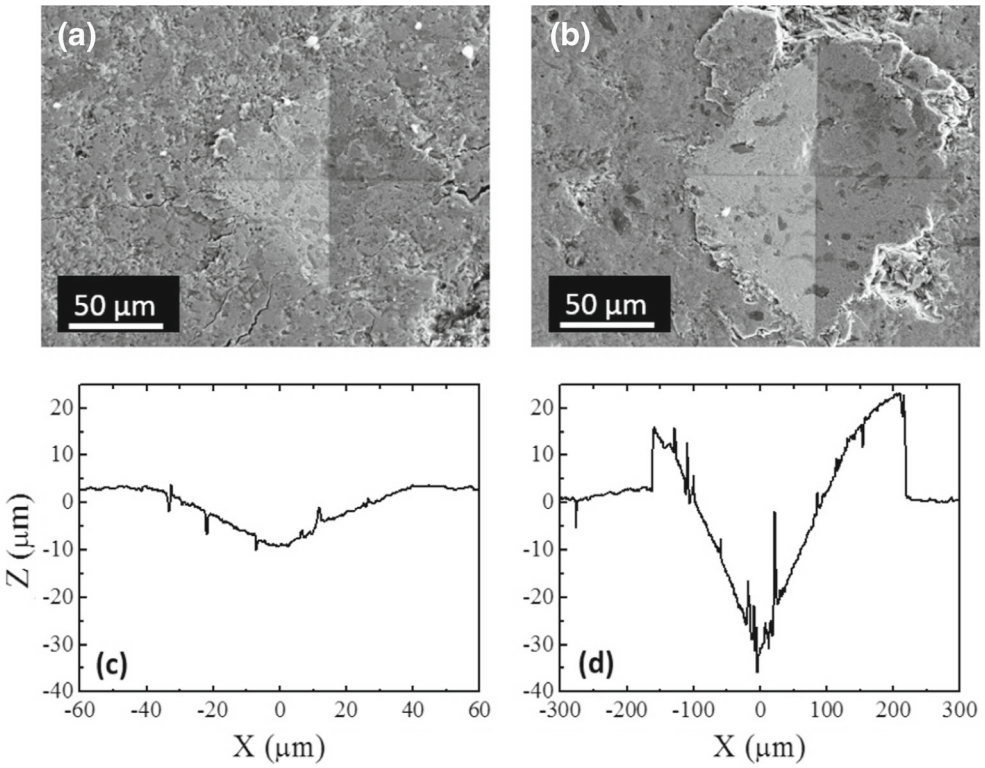

Fig. 4 Indentations marks, Vickers microhardness 2000 gf load **a** SP-0 and **b** SP-5. SEM images **c**, **d** of the indentations profile obtained by 3-D profilometer. A pile-up formation can be observed in sample SP-5. The indentations profiles were obtained in the deeper cross section of the mark

SEM observations allow us to evaluate that the ratio between diagonals of the indentation is different from 1, since these materials present texture (needle morphology and an alignment due to the pressure applied during the consolidation process) [10–12]. The average of diagonals leads to a determination, even as approximation, Vickers microhardness of the SP-0 and SP-5 samples, in 285 HV2 and 195 HV2, respectively. These results indicate a decrease in the hardness of the Bi-2223 material after the post-annealing heat treatment. SEM micrographs also confirm the decrease in the microhardness, as displayed in Fig. 4, in which one may observe a clear difference in the size of the indentation marks. Although cracks at the corners of the indentations were not clearly observed, as in other ceramic materials, a decohesion of the grains is verified [10]. Furthermore, a different indentation feature is observed when comparing the two samples (SP-0 and SP-5): they have a topography similar to those found elsewhere for a similar cuprate [11]. On the other hand, a pile up was observed in the SP-5 sample. The images and the analysis carried out by a 3-D profilometer also identified the differences, which are due the different mechanical behavior when samples are subjected to different heat treatment (see Fig. 4). The different features can be also explained by the partial melting of an intergranular amorphous phase rich in calcium, strontium, and copper and the observed infinite layer compound [7]. Experiments are underway for better clarify this particular point.

4 Conclusions

Our experimental results point out that samples of the superconducting cuprate $Bi_{1.65}Pb_{0.35}Sr_2Ca_2Cu_3O_{10+\delta}$ prepared 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 pristine material. 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 and at 750 °C, alters significantly the properties of the materials, including their mechanical properties, which are complex and need detailed investigation. However, the combined results of structural, microstructural, and magnetic properties indicated that the superconducting properties of SPS Bi-2223 samples are improved when they are subjected to a post-annealing heat treatment in air, for 5 min at 750 °C. Moreover, other sintering strategies are being evaluated to minimize the oxygen loss of samples during SPS consolidation, e.g.,

the use of steel die instead a graphite die. Finally, it is worth mentioning that the high density obtained in the SPS samples combined with their superconducting properties indicated that these SPS materials may be suitable for building devices as superconducting fault current limiters (SFCL).

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