BOLETIN DE LA SOCIEDAD ESPAÑOLA DE
Cerámica y Vidrio
ARTICULO

Ag doped $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ textured rods

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In this work, superconducting samples of $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ with Ag additions have been studied. $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ + x wt.% Ag (with x = 0, 1 and 3) powders were synthesized using a sol-gel method. The obtained powders were used as precursors to fabricate long textured cylindrical bars through a floating zone melting method. A drastic change on the microstructure has been found when comparing with undoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples. The results showed that electrical resistivity at room temperature, critical current as well as flexural strength are improved when Ag is added to these Pb doped samples, while critical temperature does not change. On the other hand, it has been found that samples with composition $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ + Ag shown E-I curves with very high sharpness values on the zone of the superconducting to normal transition, reaching n-values ($E \sim I^n$) as high as 45 at 65K.

Keywords: Superconductors, electrical properties, mechanical properties, Bi-2212, melting zone

Barras texturadas de $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ dopadas con Ag

Se han preparado polvos cerámicos de composición $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ + x % Ag en peso (con x = 0, 1 y 3) mediante un proceso sol-gel. Estos polvos se han utilizado para fabricar precursores que se texturaron por medio del método de fusión zonal flotante. Se ha encontrado un gran cambio en la microestructura cuando se compara con muestras de composición pura $Bi_2Sr_2CaCu_2O_{8+\delta}$. Tanto la resistividad eléctrica a temperatura ambiente, como la corriente crítica, así como la resistencia a flexión se mejoran cuando la Ag se adiciona a estas muestras dopadas con Pb, mientras que no se observa cambio en la temperatura crítica. Por otra parte, se ha encontrado que las muestras de composición $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ + Ag presentan una gran pendiente de la curva E-I en la zona de transición entre el estado superconductor y el estado normal. Con estas composiciones, se han encontrado valores de n ($E \sim I^n$) de hasta 45 a 65K.

Palabras clave: Superconductores, propiedades eléctricas, propiedades mecánicas, Bi-2212, fusión zonal

1. INTRODUCTION

The development of commercial applications, based on bulk high temperature superconductors, requires the use of texturing techniques in order to obtain materials with enough critical current density (J_c) values. Bi-Sr-Ca-Cu-O superconductors have demonstrated that they are suitable for technological applications when they are properly processed. An example of a texturing technique, for these Bi based superconducting bulk materials, is the laser floating zone (LFZ) technique (1, 2, 3). The superconducting materials textured using this method, have very well aligned crystals, with their a-b planes parallel to the growth direction. With this alignment, and particularly in the case of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconductors, current flow can achieve very high values without resistive losses (4). Furthermore, these textured bulk materials have very interesting properties that allow developing current leads or fault current limiters.

The application of these Bi-based textured superconductors, as fault current limiters, provides the possibility to develop resistive type ones (5). For this type of applications it is necessary the fabrication of Bi-2212 materials capable of supporting high critical current densities in the superconducting state and developing high resistance in the normal state, to effectively limit the fault current. Usually, Bi-2212 materials show a low slope of the transition from the superconducting to the normal state. As a consequence, great efforts have been put on the improvement of this slope. For this purpose, the well-know power law, $E \sim I^n$ (6), has been selected to describe the E-I curves. The fitting parameter n reflects the sharpness of the superconducting to normal transition.

One proposed solution to overcome the low slope found on the E-I curves is based on the cationic substitution, which could introduce effective flux pinning centers. In particular, the partial Pb substitution for Bi has shown to be useful to improve the intragranular pinning properties in single crystals (7, 8) and to increase the E-I curve slope in LFZ textured samples (9). On the other hand, small Ag additions have shown to be very useful in order to raise considerably the low mechanical properties of these totally melt-processed materials (10, 11).

The aim of this work is studying Bi-2212 LFZ textured rods with partial Pb substitution for Bi ($Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+\delta}$), doped with different amounts of Ag (0, 1 and 3 wt.%). The election of these Pb and Ag amounts has been determined by previous works (10, 12) which show the improvements on the Bi-2212 properties.

2. EXPERIMENTAL

$Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+\delta}$ bars, with 0, 1 and 3 wt.% Ag additions, have been prepared from commercial Bi_2O_3 (Panreac, 98+%), PbO (Panreac, 99+%), $SrCO_3$ (Panreac, 98+%), $CaCO_3$ (Panreac, 98.5+%), CuO (Panreac, 97+%) and Ag (Aldrich, 99.9+%) powders. They were weighed in the adequate atomic proportions, and, among the many different synthetic methods (13), the sol-gel method via nitrates (10) has been selected. The obtained powders were thermally treated twice at 750 and 800ºC for 12 hours with an intermediate grinding. These prereacted powders were then used to prepare cylindrical precursors, 120 mm long and 3 mm diameter, approximately, by cold isostatic pressing with an applied pressure of 200 MPa during 1 minute. The obtained cylinders were used as feed in a directional solidification process performed in a laser floating zone melting (LFZ) installation (4). The textured bars were obtained using a continuous power Nd:YAG laser (λ = 1064 nm), under air, at a growth rate of 30 mm/h and a relative rotation of 18 rpm between the seed and feed. Using these growth conditions and adjusting the laser power input to obtain a melted zone of approximately 1-1.5 times the rod diameter, it is possible to obtain stable growth, which allows the fabrication of very homogeneous bars.

The material presents an incongruent melting and, in consequence, after texturing, it is necessary to perform a thermal treatment in order to form the Bi-2212 superconducting phase (14). This annealing process is performed under air, and consisted in two steep: 60 h at 845ºC followed by 12 h at 800ºC and, finally, quenched in air to room temperature. Before thermal treatment, silver contacts were painted on the as-grown samples. After annealing, the silver contacts have typical resistance values below 1$\mu\Omega$.

The samples used for the electrical characterization were approximately 4 cm long. Standard four-probe configuration was used for electrical measurements. Resistivity measurements have been performed between 77 and 273K, using a dc current of 1 mA. The E-I characteristics of the annealed rods have been determined between 65 and 77 K. From these results, the variation of the slope of the E-I curves as a function of the temperature, in the range 1-10 μV/cm, was determined using the power law $E \sim I^n$.

Transverse and longitudinal cross-sections of the samples were cut and mechanically polished to be studied by scanning electron microscopy (JEOL JSM 6400) equipped with an energy dispersive spectroscopy (EDX) system.

Mechanical characterization was performed by flexural strength, using the three-point bending test in a Instron 5565 machine with a 10 mm loading span fixture and a punch displacement speed of 30 μm/min.

In order to study the influence of Pb doping, all these results are also compared with pure Bi-2212 samples grown and thermally treated in the same conditions used for the Pb doped ones.

3. RESULTS AND DISCUSSION

Typical microstructure obtained in pure Bi-2212 textured bars show a dense and compact microstructure due to the low porosity found in these samples. Moreover, they show a well aligned Bi-2212 grains, with their c-axis nearly perpendicular to growth direction, and very small amount of secondary phases (4). This is a good result when having into account that the quaternary Bi_2O_3-SrO-CaO-CuO system shows more than 20 stable phases (15). In this very complex system minor compositional variations may cause major changes in the obtained phases.

A drastic microstructural change can be found when Pb is added, as can be observed in figure 1, where two SEM micrographs obtained on longitudinal polished samples of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (figure 1a) and $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+\delta}$ (figure 1b), before annealing. In this figure it can be clearly observed the increased misorientation on the ceramic grains induced by Pb addition. This drastic change on the microstructure, induced by the Pb doping, can be explained by the increased complexity of the quinary Bi_2O_3-PbO-SrO-CaO-CuO system. In this case, besides a significant Pb solubility of the bismuth-containing phases up to several weight per cent, two plumbates could appear, which are Ca_2PbO_4 and $Pb_4Sr_5CuO_{10}$ (451 phase), adding more complexity to the system, not only for the presence

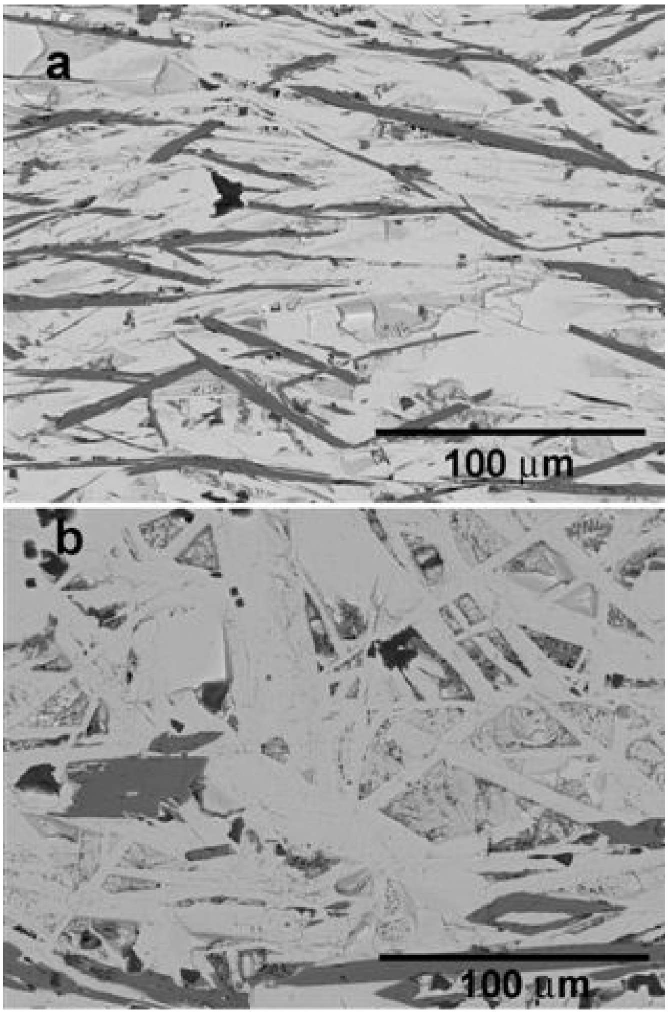

Fig. 1- Longitudinal SEM images obtained on as grown polished samples. a) $Bi_2Sr_2CaCu_2O_{8+\delta}$; and b) $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+\delta}$.

of these two new phases but for the destabilization of the other phases. This ternary oxide can dissolve important amounts of Bi and Ca, giving phases with different stoichiometries, which can be represented by the (Pb+Bi):Sr:Ca:Cu ratio 3221.

Figure 2 shows the microstructural evolution on the annealed $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+\delta}$ samples as a function of Ag content, determined on transversal polished sections. In this figure is displayed the backscattered (left) and secondary (right) electron micrographs, in order to distinguish the holes from the secondary phases. As it can be easily deduced from the SEM micrographs, Ag addition improves the microstructure. It can be observed that the amount of holes and secondary phases decreases when Ag content increases from 0 to 1 and 3 wt.% (figures 2a, 2b and 2c, respectively). Moreover, the spatial defect distribution changes when Ag increases, showing a higher concentration of holes and secondary phases in the center of the samples, leaving a thicker outer region free of defects.

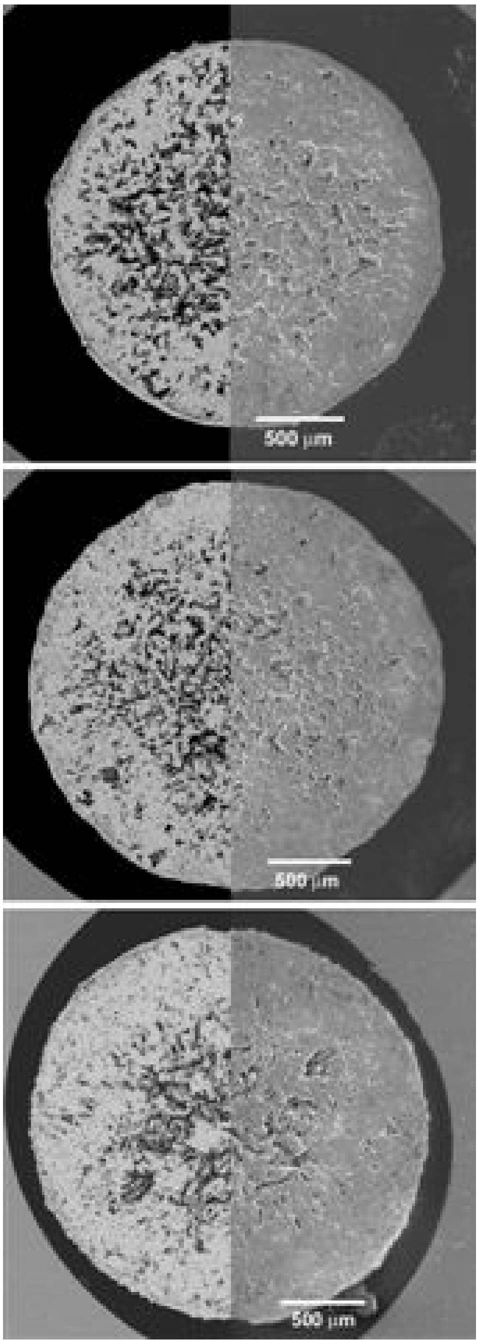

Fig. 2- Transversal backscattered (left) and secondary (right) SEM images of polished samples after grown and annealing. a) 0 wt.% Ag; b) 1 wt.% Ag; c) 3 wt.% Ag. The darker contrasts are defects composed by Bi-free secondary phases and holes between superconducting grains in the backscattered images and, only holes for the secondary ones.

The observed pernicious effect of Pb on the microstructure of the samples is also reflected on their electrical properties, for instance T_c. Typical T_c values on undoped Bi-2212 samples are usually around 90K (4). When Pb is partially substituting Bi, it is found a significant decrease of T_c to values around 82K. This decrease on the T_c values confirms the results reported in previous works (16). On the other hand, Ag doping has no effect on the T_c values, as can be observed in figure 3, where the resistivity as a function of temperature is plotted for samples with different Ag contents.

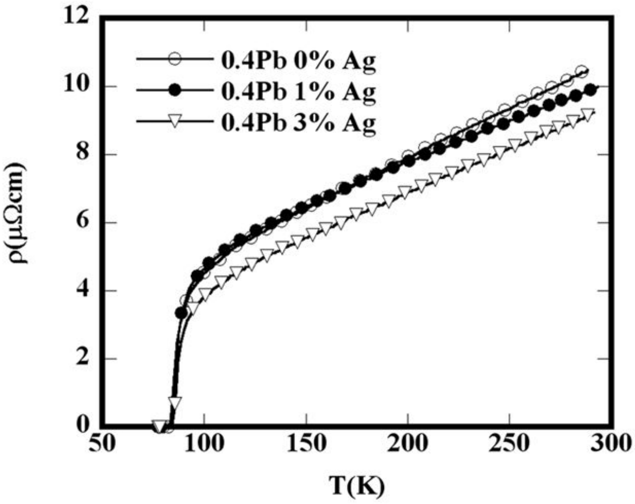

Fig. 3- Electrical resistivity (1mA dc current) measured between 77K and room temperature.

The effect of Ag addition on the resistivity of these samples can be clearly seen on this figure. For instance, at T=273K the resistivity values decrease from 10.0 $\mu\Omega$.cm for samples with 0 wt.% Ag, to 9.5 $\mu\Omega$.cm for samples with 1 wt.% Ag and, finally, to 8.7 $\mu\Omega$.cm for samples with 3 wt.% Ag. This effect is associated with an improvement of the grains connectivity due to the presence of a good metallic conductor, as Ag, between the ceramic grains (10), without changing their size and orientation.

This beneficial effect due to the Ag doping is also observed on the evolution of I_c as a function of the temperature. In figure 4, the reduced critical current, normalized to the value of I_c(77K) for the sample without Ag, is represented. It has been found that the critical current at 77K for the sample with 1wt.% Ag is around 15% higher than the obtained values for samples without Ag, and can reach an increase of about 40% when 3 wt.% Ag is added. This behaviour is correlated with the fact that in these materials lower resistivity values at room temperature yield higher I_c (17). The observed relative difference in the measured critical current is found for all the studied temperature range (65-77K).

Despite of the negative influence of Pb on the microstructure and transport properties of these LFZ textured rods, it is well known that Pb can modify the sharpness of the superconducting to normal transition in the E-I curves (12, 18).

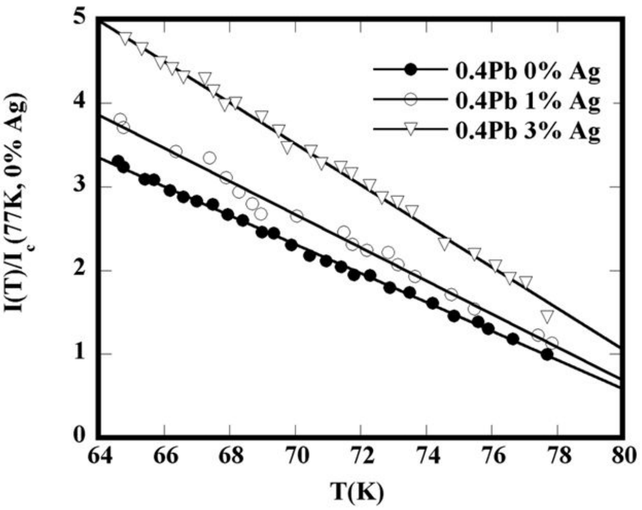

Fig. 4- Reduced critical currents for Pb doped samples, between 65 and 77K, normalized to the value of I_c(77K) for the sample without Ag.

To analyze this effect, the slope values (n) have been measured from the E-I curves. In figure 5 typical normalized fitted E-I curves, between 1-10μV/cm, are displayed for undoped and Pb doped samples. As it can be observed in this figure, Pb addition leads to a spectacular increase of the fitted n-value, from 7 to 13 at 77K (nearly 200%). The slope of the transition is even sharpness at lower temperature, as it is reflected in that figure, where the E-I curve for Pb doped sample at 65K is also included. In this work, n-values as high as 45 are found for Pb doped samples at 65K, independently of Ag content. From the experimental results, it seems that Ag has not influence on this superconducting parameter. Nevertheless, the n-values determined in this work are the highest values reported in the literature for Bi-2212 bulk compounds in this range of E-I curves, to the best of our knowledge.

Finally, mechanical properties for these materials have been studied due to their importance for practical applications. Flexural strength has been determined using the three point bending test. Mechanical characteristics of the samples, as a function of Ag content, are summarized in table 1. At least, ten bending tests have been performed for each composition. From these results, mean values and standard errors were calculated. The results displayed in table 1 show that the addition of 3 wt.% Ag is improving flexural strength in about 30%, when compared with the 0 wt.% Ag one. On the other hand, the addition of 1 wt.% Ag, does not change appreciably the mechanical strength. The improvement of the measured mechanical strength is related with the porosity reduction and its distribution. For this reason, in lower porosity samples, as Pb free Bi-2212, it has been found that the optimum Ag content was only 1 wt.% (10). In this work, the porosity has been increased by the Pb presence, as previously discussed. In this case, the optimum Ag amount is higher in order to fill the bigger amount of porosity, reaching values of 3 wt.%. However, it should be noted that samples textured by LFZ, which are totally melted, have a low porosity as compared with textured samples obtained by partial melting processes, where Ag content, to improve mechanical properties, can reach values as high as 20 wt.% (19).

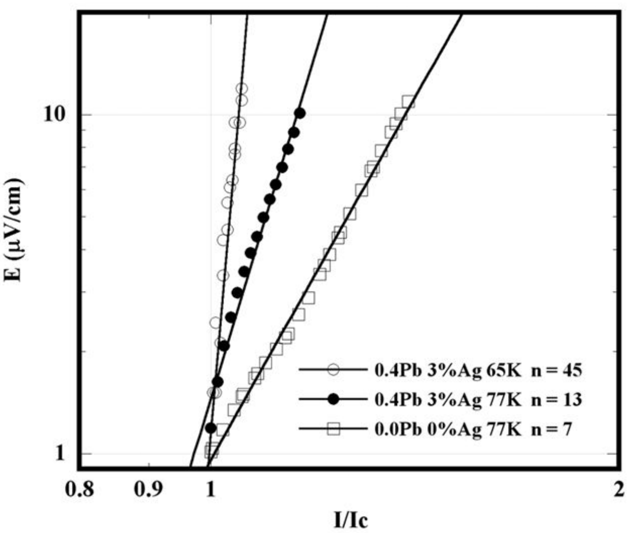

Fig. 5- E-I curves, measured between 1-10 μV/cm, for the sample $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+\delta}$ + 3 wt.% Ag, highlighting the high n values obtained, as compared with a Bi-2212 sample (free of Pb and Ag).

TABLE I.- FLEXURAL BENDING STRENGTH AND STANDARD ERROR AS A FUNCTION OF AG CONTENT

% wt. Ag	σ_f (MPa)
0	71 ± 6
1	69 ± 3
3	93 ± 3

4. CONCLUSIONS

Samples with nominal $(Bi_{1.6}Pb_{0.4})Sr_2CaCu_2O_{8+\delta}$ + x wt.% Ag (with x = 0, 1 and 3), have been textured using the floating zone melting process, and subsequently annealed to develop the superconducting Bi(Pb)-2212 phase. In all the cases, critical temperatures are higher than 77K when Pb is added. The addition of Ag improves the microstructure of these Pb partially substituted Bi-2212 samples.

Electrical and mechanical measured properties for Pb-doped samples are lower than those obtained for the pure Bi-2212, as it was found in the microstructure. Ag addition improves these properties, reaching the best values for samples with an Ag content of 3 wt.%.

Pb addition has a beneficial effect on the sharpness of the E-I curve, n-values can increase spectacularly when compared with undoped Bi-2212 samples. In this case Ag addition has a negligible effect on this superconducting parameter. High n-values of 13 for 77K and 45 for 65K have been found. These values are the highest reported in the literature, in the E measured range of 1-10 μV/cm, in the knowledge of the authors.

ACNOWLEDGEMENTS

The authors are indebted the Spanish Ministry for Education and Science (MAT 2005-06279-C03-01) and to the Aragón Regional Government (Consolidated Research Groups E03 and T12) for financial support. The technical help of C. Gallego, R. Lou, C. Estepa and J. A. Gómez are acknowledged.

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Recibido: 31.07.07
Aceptado: 20.12.07