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Study of the variation of the E-I curves in the superconducting to normal transition of Bi-2212 textured ceramics by Pb addition

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Vitreous cylinders with compositions $Bi_{2-x}Pb_xSr_2CaCu_2O_y$, (x = 0, 0.2, 0.4 and 0.6) were prepared and used as precursors to fabricate textured bars through a laser floating zone melting method (LFZ). The resulting textured cylindrical bars were annealed, followed by their electrical characterization. The microstructure was determined and correlated with the electrical measured properties. The influence of Pb doping on the sharpness of the superconducting to normal transition on the E-I curves has been determined. The sharpest transitions have been obtained for samples doped with 0.4Pb.

Keywords: Bi-2212, superconductivity, electrical properties, Pb.

Variación de las curvas E-I en la transición normal superconductor de cerámicas texturadas BI-2212 por adición de PB.

Se han preparado precursores de tipo vítreo en forma de cilindro con composiciones nominales $Bi_{2-x}Pb_xSr_2CaCu_2O_y$, con x = 0, 0.2, 0.4 y 0.6. Estos cilindros se han utilizado como precursores para fabricar barras texturadas por medio de una técnica de fusión zonal inducida por láser (LFZ). Estas barras texturadas se recocieron a diferentes temperaturas y se caracterizaron eléctricamente. Además, se examinó su microestructura para correlacionarla con las propiedades eléctricas medidas. La variación de la transición del estado superconductor al normal se ha relacionado con el dopaje con Pb a través de las curvas E-I. Las mejores transiciones se han obtenido para muestras dopadas con 0.4 Pb..

Palabras clave: Bi-2212, superconductividad, propiedades eléctricas, Pb.

1. INTRODUCTION

The development of commercial applications on high temperature superconductors requires the use of texturing techniques in order to obtain bulk materials with the electrical properties that are required for technological applications[1]. $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconductors have demonstrated that they are suitable for many applications when they are properly processed. An example of a texturing technique for Bi-2212 bulk materials is the Laser Floating Zone (LFZ) technique[2]. The superconducting materials textured by this technique have very interesting properties[3] that allow developing current leads[4] or fault current limiters[5]. One of the main advantages of this method is that the materials can be rapidly grown due to the large thermal gradients present at the solid-liquid interface[6]. Furthermore, the LFZ technique has shown to be useful to obtain good textured samples in other systems[7,8].

However, the low slope of the superconducting to normal transition on the electrical current curve, E-I, imposes severe limitations for their application as fault current limiters. The usual solution to overcome this problem is based on the use of samples with long lengths. Another possible way is the cationic substitution, which could introduce effective flux pinning centers and increase the slope of the E-I curves.

The partial Bi substitution with Pb has shown to be useful to increase the intragranular pinning properties in single crystals, leading to the enhancement of both irreversibility field and critical current density[9,10]. Furthermore, it has been found to decrease the anisotropy at high temperatures[11]. In these Pb-doped crystals it is well established the existence of two alternating Bi(Pb)-2212 phases[12]. One, the so-called α phase, exhibits a modulated structure with a nominal Pb content of ~ 0.4[12]. The other one, the β phase, is a modulated-free structure and has higher Pb content, around 0.6[12]. The α phase exhibits a one-dimensionally modulated structure along the b axis in which atomic positions are displaced in a wavy manner. The interfaces between the two phases are extended planar defects, which act as strong flux pinning centers[12]. More recently, it has been found that the β phase (modulation-free phase) enhances pinning due to its lower anisotropy. In fact, the best pinning properties are exhibited by the combination of a dominant β phase strengthened by α/β interphase[10]. This optimal phases combination has been obtained for 0.33 effective Pb substitution[10].

Contrarily to the results obtained for single crystals, limited success is obtained in bulk and tape systems with this cationic doping [13-15]. The aim of this work is to study the influence of Pb doping on the sharpness of the superconducting to normal transition on the E-I curves in LFZ textured Bi-2212 thin bars. For this purpose, the well-known power law, $E \sim I^n$, has been selected to describe the E-I curves. The fitting parameter n reflects the sharpness of the superconducting to normal transition and it is correlated with the quality of the superconducting material.

2. EXPERIMENTAL

$Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ precursors, with x = 0, 0.2, 0.4 and 0.6 have been prepared from commercial Bi_2O_3 (Panreac, 98+%), PbO (Panreac, 99+%), $SrCO_3$ (Panreac, 98+%), $CaCO_3$ (Panreac, 98.5+%) and CuO (Panreac, 97+%) powders. They were weighted in the adequate atomic proportions, mixed in a ball mill and thermal treated twice under air (12h at 750 and 780 ºC) to decompose the carbonates and decrease the volume of the mixture (about 50% in the first step and 35% in the second). This prereacted mixture was then introduced into a Pt crucible and melted at 1050-1075 ºC to assure good homogeneity and fluidity of the liquid. The obtained melt was then quenched into silica tubes, 2 mm inner diameter, to obtain long (up to 25 cm) and homogeneous cylindrical bars[16]. The vitreous bars were used as feed in an LFZ melting system[3], using a Nd-YAG laser (λ = 1064 nm). The growth speed was fixed at 40 mm/h with a rotation of 15 rpm, to obtain a homogeneous melted zone. In these stable conditions, it is possible to obtain long textured bars with final diameters between 1.8 and 1.9 mm.

After texturing, samples were thermally characterised by DTA at 10 ºC/min, in an Universal V3.7A TA Instruments, to determine the melting point and, consequently, fix the upper limits for the annealing temperatures. To perform the electrical measurements silver contacts were painted on the as-grown samples. In order to form the Bi-2212 phase and, at the same time, ensure good electrical connectivity between the silver contact and the textured ceramics, a two-step annealing process in air was performed: 60h at temperatures between 805 and 835 ºC, followed by 12h at 800 ºC. In all the cases they were quenched to room temperature. After thermal treatments, the resulting silver contacts were characterised, obtaining resistances below 1$\mu\Omega$. The E-I characteristics at 77 K of the annealed rods have been measured on 4 cm length samples by the standard four-probe configuration. From these measurements, the slope of the E-I curves has been determined in the range of 1 ~ 10 μV/cm using the power law E ~ I^n. The resistivity as a function of temperature was measured from 77 K to room temperature, using a dc current of 1 mA. From these measurements the critical temperature, T_c, was determined.

Present phases, their composition, alignment and distribution, as well as element mapping on as-grown and annealed samples were determined using a JEOL 6000 SEM microscope provided with an energy dispersive spectroscopy (EDX) system.

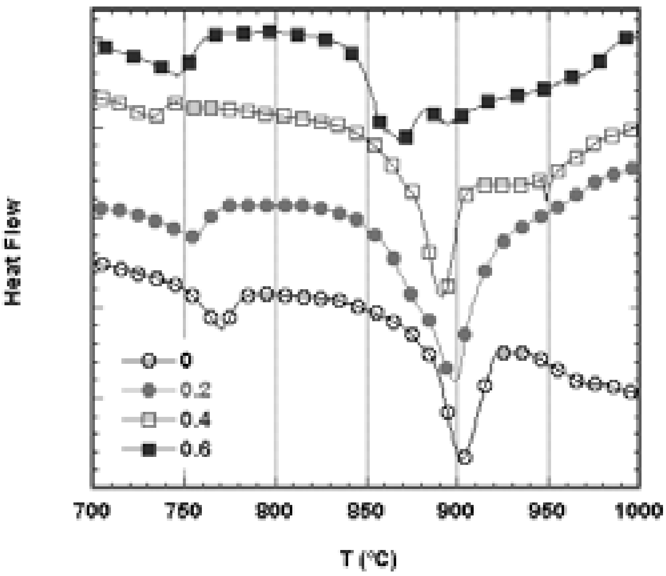

Fig. 1- DTA plots of as grown samples with different nominal Pb contents (0, 0.2, 0.4 and 0.6) measured at 10 ºC/min.

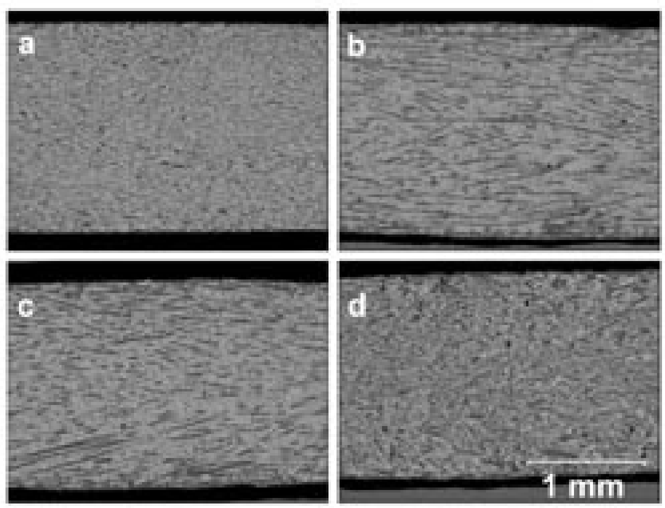

Fig. 2- Longitudinal SEM micrographs, showing a general view of the as grown samples for nominal x = 0 (a), 0.2 (b), 0.4 (c), and 0.6 (d), respectively. Bi-free phases are shown as dark contrast.

3. RESULTS AND DISCUSSION

Analysis of the precursor vitreous materials through SEM micrographs and EDX element mapping shows that the starting material is very homogeneous along the bars. After characterisation, the vitreous precursors were textured by a LFZ technique described elsewhere[3]. To determine melting temperature of as-grown materials, thermal analyses were performed. The melting point has been determined from the second endothermic peak. As it can be seen in figure 1, on textured materials, the melting temperature decreases when Pb nominal content increases. On the other hand, this peak for samples with x = 0.6 shows a different behaviour when compared with samples with lower Pb contents.

Figure 2 shows SEM micrographs of the longitudinal section of the as grown samples for different Pb contents. Focusing attention on grain sizes and orientation of Bi-free secondary phases (dark gray contrast), the grain orientation seems to be improved when nominal Pb content increases from 0 to 0.2 and 0.4. Higher Pb content leads to a dramatic reduction of the orientation of these phases. In undoped LFZ samples the Bi-free grains are the primary solidification phases[17] and they induce the orientation in the superconducting phases. For this reason, the texture of the superconducting phases is strongly conditioned by their orientation. However, the addition of different cations can disturb the crystal growth habit[18] leading to the misorientation of the Bi rich crystals (light gray contrast). This effect is shown in figure 3, where higher magnification micrographs are presented. As can be clearly seen, the undoped sample exhibits the best texture regarding Bi-rich phases, which are the origin of the superconducting phases. When Pb is present, a misalignment of these phases is

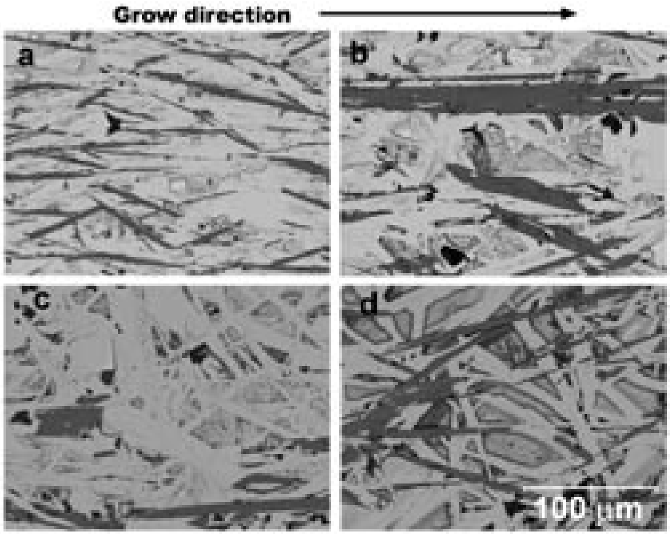

Fig. 3- Longitudinal SEM micrographs, showing a detail of the centre of the as grown samples for nominal x = 0 (a), 0.2 (b), 0.4 (c), and 0.6 (d), respectively. The Bi-rich phases (lightest contrast, 2201 phase) show a misalignment from the grow direction when Pb is present.

produced and they tend to grow perpendicularly to the growth direction, which can lead to a decrease on the superconducting properties. EDX analyses show that Pb is always associated to Bi.

In order to develop the superconducting Bi-2212 phase an annealing has been performed on textured samples. This thermal treatment consists in a two-step process according to previous work on undoped LFZ Bi-2212 rods[19]. For undoped samples the highest treatment temperature is around 870 ºC. However, for Pb-doped samples this temperature is reduced accordingly following the lead content as can be see in figure 1. The chosen conditions have been T_{tr} (60 h) + 800ºC (12 h) + quench to room temperature[10]. To compare all the compositions, all the samples were treated at the same temperatures. As a consequence, the maximum T_{tr} temperature was 835 ºC, wich is the maximum treatment temperature for samples with x = 0.6, higher temperatures lead to the melt of these Pb-rich samples. The minimum T_{tr} was 805 ºC, a temperature that preserves the (Bi,Pb)-2212 modulated structure (α phase)[12]. In order to compare the influence of this T_{tr} on the final electrical properties, two additional T_{tr} have been used, 815 and 825 ºC. The values of critical temperatures determined from resistivity measurements were always higher than 81K, showing that any of the thermal treatments performed on the samples have been sufficient to develop the Bi-2212 superconducting phase as the main phase.

After annealing, the typical obtained microstructures are shown in figure 4. The present phases in all the samples are: Bi(Pb)-2212 (gray contrast), Bi(Pb)-2201 (light grey), and $(Sr,Ca)CuO_2$ (black). In doped samples, two new phases appear, identified as plumbate/like phase, with composition $(Bi,Pb)(Sr,Ca)O_x$ (dark gray), and $(Sr,Ca)_{14}Cu_{24}O_{41}$ (14:24, light black). The plumbate phase grows in size and volume fraction with Pb content. It has been observed that the aggregates size can reach more than 1 mm long for Pb contents of 0.6. This is an undesirable phase mainly for two reasons: first, it takes Bi, avoiding the formation of the superconducting phase and second, its formation is going to break the superconducting

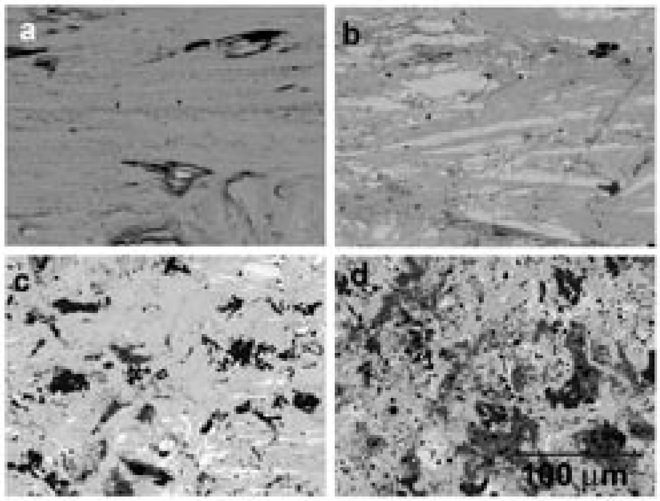

Fig. 4- Longitudinal SEM micrographs, showing a detail of the centre of the annealed samples for nominal x = 0 (a), 0.2 (b), 0.4 (c), and 0.6 (d), respectively. The plumbate-like phases (dark contrast) increase with Pb content destroying the superconducting path.

grains connectivity. One possible solution proposed in the literature to avoid the formation of this phase resides on the thermal treatment under reduced oxygen partial pressure[13,14].

After anneling, samples were electrically characterized. Figure 5 shows the electrical resistivity measurements, from 77 K to room temperature, on annealed samples at 805 ºC. As it can be seen, T_c of the doped samples is lower than that of the undoped. This behaviour is observed for all the annealing temperatures, in agreement with previous work in single crystals[12] and tapes[13]. The T_c values obtained for these LFZ textured samples are ranging from 81 to 91 K.

In figure 5 it is also observed that the resistivity of the x = 0.2 and x = 0.4 Pb-doped samples is slightly higher than that for the undoped. On the other hand, for x = 0.6 a big increase in this magnitude is observed. Accordingly with

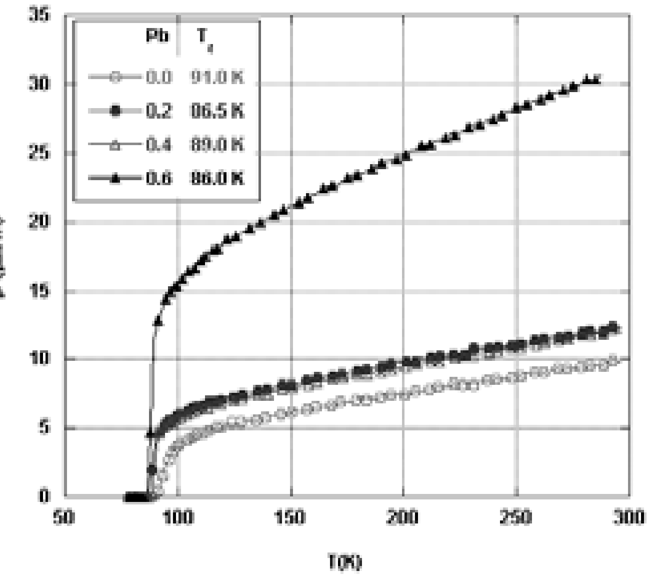

Fig. 5- Resistivity measurements of samples annealed at T_{tr} = 805 ºC. Critical temperatures deduced from the curves are displayed for each nominal composition.

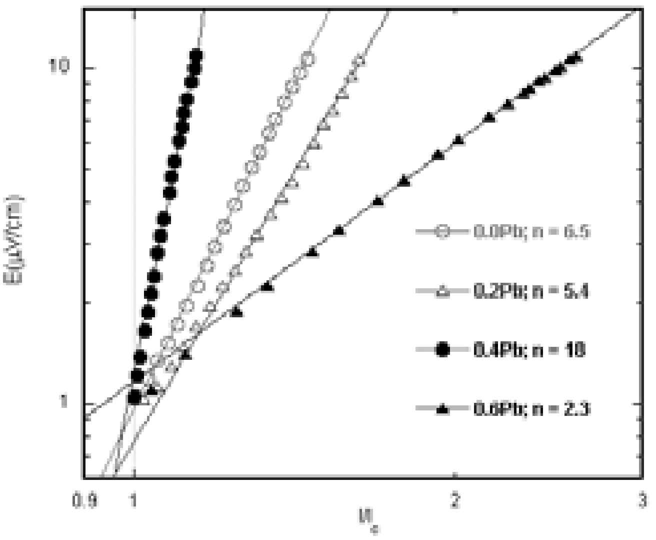

Fig. 6- Normalized fitted E-I curves between 1 and 10 μV/cm for samples annealed at T_{tr} = 835 ºC. n values determined from the fitting are displayed for each nominal composition.

the microstructure of the annealing samples (figure 4), this behaviour can be related with the amount of secondary phases, principally plumbates, and with their ability to reduce the effective area for the transport electrical current. Any work concerning with the improvement on transport current capability must reduce these secondary phases with an adequate material processing.

Typical E-I curves are plotted in figure 6 for all the compositions. To clarify the graphical representation normalized current has been used and fitted using the power law to determine the n-values. The effect of Pb addition is a reduction of the n-values except in the case of 0.4 Pb, where a spectacular increase has been obtained. This tendency is found for all thermal treatments. The different n-values obtained for 0.4 Pb-doped samples are displayed in table I. Typical values for Bi-2212 are lower than 10, while for Bi-2223 can reach values as high as 20. It is clear that for LFZ textured samples with Pb content of 0.4 the obtained n-values are higher than those found for Bi-2212 and they are in the range of Bi-2223.

All the shown results for Pb substitution point out to a worse microstructure and, consequently, to a reduction of the electrical characteristics. This tendency gives, as a consequence, a reduction of the n-values when Pb content increases. An exception to this tendency is found when Pb content is 0.4, where the highest n-values are obtained. This is related with the effective Pb content in the Bi-2212 grains. When SEM-EDX is performed on the samples, maximum Bi effective substitution of about 0.34 Pb is found for samples with nominal composition of 0.4 Pb. On the other hand, samples with nominal compositions of 0.2 and 0.6 Pb reach a maximum effective substitution of 0.13 and 0.20, respectively. This result is in agreement with previous works, where the best superconducting properties are obtained for effective Pb substitution of 0.33 Pb[10].

TABLE I. *n* VALUES OBTAINED FOR NOMINAL 0.4 PB DOPED SAMPLES FOR EACH T_{TR} TEMPERATURE.

T_{tr} (ºC)	805	815	825	835
n	10	18	14.4	16.2

4. CONCLUSIONS

Bulk samples of Bi-2212 with different amounts of Pb have been prepared and textured by an LFZ process. After different annealing procedures superconducting behaviour has been obtained in all the cases. All results show that increasing Pb content, for the performed thermal treatments, the microstructure and, consequently, superconducting properties are deteriorated. This behaviour is related to the formation of plumbate like phases, which disrupt the superconducting path and substray cations from the nominal Bi-2212 composition.

Only on the case of nominal 0.4 Pb content, an improvement on the n-value, has been found. This great enhancement is related to the highest Pb content inside the Bi-2212 grains, reaching 0.34, which is very close to the optimal value found, 0.33 Pb.

More work is been conducted on the annealing conditions of these bulk samples in order to avoid the presence of the plumbate like phases and to enhance the global superconducting properties.

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